Supplementary Information Section

Controlling Molecular Mobility in Polymer Matrices: Synchronizing Switching Speeds of Multiple Photochromic Dyes

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Materials

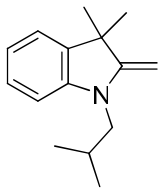
Hydroxy-terminated poly(dimethylsiloxane) starting materials were purchased from Gelest, Inc. All other reagents were purchased from Aldrich and used as supplied, unless stated otherwise. 1-(4-Dimethylaminophenyl)-1-phenyl-prop-2-yn-1-ol, 1,1-Bis(4-dimethylaminophenyl)-prop-2-yn-1-ol, 1-Phenyl-1-(4-piperidinophenyl)-prop-2-yn-1-ol, 1,1-Bis(4-dimethoxyphenyl)-prop-2-yn-1-ol and 1-Phenyl-1-(4-dimethylaminophenyl)-prop-2-yn-1-ol were synthesized from the corresponding benzophenones using the procedure of Gabbutt *et al.*[1] 9'-Hydroxy-1,3,3-trimethyl-spiro[indoline-2,3'[3*H*]naphtho[2,1-*b*][1,4]oxazine],[2] 6'-Piperazine-1,3,3-trimethyl-spiro[indoline-2,3'[3*H*]naphtho[2,1-*b*][1,4]oxazine],[3] 2,2-Bis(4-methoxyphenyl)-5-(2-hydroxyethoxycarbonyl)-6-phenyl-[2*H*]-naphtho[1,2-*b*]pyran[4] and 3,3-Bis(4-methoxyphenyl)-13-hydroxy-indeno[2,1-*f*]naphtho[1,2-*b*]pyran[5] were

synthesized using the literature procedures. Mono end-functional photochromic dye-poly(dimethylsiloxane) conjugates (**2**, **5**, **8**, **11**, **14**, **17**, **20**, **23**, **26**, **29**) and control compounds (**3**, **6**, **9**, **12**, **15**, **18**, **21**, **24**, **27**, **30**, **36**) were synthesized using identical reaction conditions to those described elsewhere.[6]

Conjugatable Photochromic Dye Starting Materials

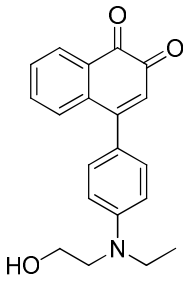
1,3-Dihydro-1-isobutyl-3,3-dimethyl-6'-(4-(*N*-ethyl, *N*-(2-hydroxyethyl)amino) phenyl)-spiro-[2*H*-indole-2,2'[2*H*]naphth[1,2-*b*][1,4]oxazine]. This compound was synthesized using the literature procedure[7,8] outlined below, and is an analogue of a photochromic dye from the patent literature.[9]

(a) 1-Isobutyl-3,3-dimethyl-2-methyleneindoline



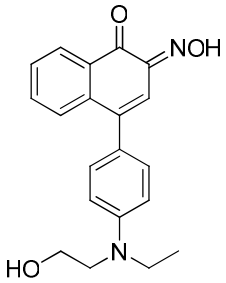
A mixture of 2,3,3-trimethylindolenine (3.15 g, 19.78 mmol) and 1-iodo-2-methylpropane (3.44 mL, 29.70 mmol) in 1,4-dioxane was heated in a sealed tube at 115°C for 72 hours. The mixture was then cooled, poured into Et_2O (150 mL) and the liquors decanted. The residue was then washed with three further portions of Et_2O and dried *in vacuo*. The residual hygroscopic purple glass was suspended in H_2O (100 mL), treated with KOH (1.12 g, 19.83 mmol) and stirred rapidly at room temperature for 30 mins. The mixture was extracted with Et_2O (×3), dried with Na_2SO_4 and evaporated to a brown oil which was purified by column chromatography eluting with 0-10% v/v EtOAc/petroleum ether, affording the title product as an orange oil (1.28 g, 30%), which was stored in a freezer until used. ^{1}H NMR (200 MHz) δ 7.14-7.06 (m, 2H), 6.74 (t, *J* = 7.7 Hz, 1H), 6.54 (d, *J* = 7.6 Hz, 1H), 3.85 (dd, *J* = 1.8, 8.7 Hz, 2H), 3.29 (d, *J* = 7.5 Hz, 2H), 2.21 (septet, *J* = 6.9 Hz, 1H), 1.34 (s, 6H), 0.95 (d, *J* = 6.7 Hz, 6H) ppm.

(b) 4-(4-(*N*-ethyl, *N*-(2-hydroxyethyl)amino)phenyl)naphthalene-1,2-dione



A suspension of 1,2-napthoquinone-4-sulfonic acid sodium salt (10.5 g, 40.35 mmol) in a 9:1 mixture of water:methanol (250 mL) was treated in one portion with 2-(ethyl(phenyl)amino)ethanol (6.67 g, 40.35 mmol) and stirred at 50°C for 18 hours. The mixture was then cooled, the methanol removed *in-vacuo* and the resulting suspension filtered. The precipitate was then washed with water and oven dried at 50°C to give the title product as a dark purple solid (6.8 g, 54%). MPt: 163°C (dec). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 1.3, 7.5 Hz, 1H), 7.61-7.50 (m, 3H), 7.40 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.43 (s, 1H), 3.89 (q, *J* = 3.9 Hz, 2H), 3.60-3.50 (m, 4H), 1.63 (t, *J* = 5.7 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H) ppm.

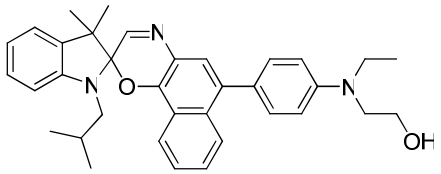
(c) 4-(4-(*N*-ethyl, *N*-(2-hydroxyethyl)amino)phenyl)-2-(hydroxyimino) naphthalen-1(2*H*)-one



A suspension of 4-(4-(*N*-ethyl, *N*-(2-hydroxyethyl)amino)phenyl)naphthalene-1,2-dione, step (b), (8.5 g, 26.48 mmol) in absolute ethanol (150 mL) was treated in one portion with hydroxylamine hydrochloride (3.68 g, 52.96 mmol, recrystallised from 75:25 EtOH : H_2O) and stirred at RT for 2 hours. The solvent was then evaporated *in-vacuo* and the residue suspended in H_2O (500 mL). The aqueous phase was basified to pH 10 with ammonium hydroxide solution and extracted into EtOAc (×4). The

combined organics were then dried (Na_2SO_4) and evaporated *in-vacuo* to afford the title compound as a dark red solid (9.1 g, >95%). MPt: 180-181°C. ^{1}H NMR (200 MHz, d_6-DMSO) δ 8.12 (d, *J* = 7.6 Hz, 1H), 7.71-7.40 (m, 3H), 7.25 (d, *J* = 8.5 Hz, 2H), 6.90 (s, 1H), 6.76 (d, *J* = 8.6 Hz, 2H), 3.60-3.30 (m, 6H), 1.10 (t, *J* = 6.8 Hz, 3H) ppm. MS (EI): *m/z* 336.2 [M^+].

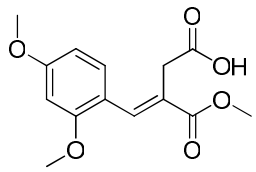
(d) 1,3-Dihydro-1-isobutyl-3,3-dimethyl-6'-(4-(*N*-ethyl, *N*-(2-hydroxyethyl)amino)phenyl)-spiro-[2*H*-indole-2,2'[2*H*]naphtha[1,2-*b*][1,4]oxazine]



A suspension of 4-(4-(*N*-ethyl, *N*-(2-hydroxyethyl)amino)phenyl)-2-(hydroxyimino)naphthalen-1(2*H*)-one (1.2 g, 3.57 mmol) in anhydrous ethanol (20 mL) was treated with 1-isobutyl-3,3-dimethyl-2-methyleneindoline, step (a), (0.99 g, 4.64 mmol) in one portion and heated to 100°C in a sealed tube for 3 hours. The resulting mixture was then evaporated *in-vacuo* and the residue purified by column chromatography eluting with 10-50% v/v EtOAc/petroleum ether to afford the title product as a light green colored foam (1.6 g, 84%). MPt: 180-183°C (dec.). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.06-7.89 (m, 2H), 7.73 (s, 1H), 7.46 (s, 1H), 7.39-7.29 (m, 4H), 7.19 (dd, *J* = 1.2, 7.6 Hz, 1H), 7.10 (d, *J* = 6.4 Hz, 1H), 6.91-6.81 (m, 3H), 6.62 (d, *J* = 7.8 Hz, 1H), 3.89 (q, *J* = 5.8 Hz, 2H), 3.58-3.45 (m, 4H), 3.10-2.80 (m, 2H), 2.19-2.00 (m, 1H), 1.39 (d, *J* = 2.1 Hz, 6H), 1.24 (t, *J* = 7.0 Hz, 3H), 0.95 (dd, *J* = 6.6, 10.6 Hz, 6H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$) 153.1, 147.8, 147.4, 140.5, 135.7, 133.1, 132.9, 131.1, 128.3, 127.8, 126.7, 126.3, 125.4, 123.8, 122.1, 121.6, 119.4, 112.6, 107.1, 100.1, 60.3, 52.8, 52.6, 51.9, 45.7, 28.0 and 25.1. MS (EI): *m/z* 533.3 [M^+]; (HR, EI): *m/z* 533.3020 ($C_{35}H_{39}N_3O_2$ requires: 533.3037).

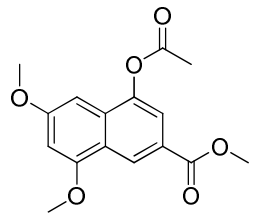
2-(4-Dimethylaminophenyl)-2-phenyl-5-hydroxymethyl-7,9-dimethoxy-2*H*-naphtho[1,2-*b*]pyran. This compound was synthesized using the literature procedure[10] with some modifications.

(a) 4-(2,4-Dimethoxyphenyl)-3-methoxycarbonyl-3-butenenoic acid



2,4-Dimethoxybenzaldehyde (10.0 g, 0.06 mol), dimethylsuccinate (8.79 g, 0.06 mol) and *t*-BuOK (8.0 g, 0.072 mol) were mixed thouroughly with a mortar and pestle. The reaction mass turned to a sticky yellow tar. The mixture was left at RT for 2 hours with occasional stirring until no starting material was visible by TLC. The mixture was then dissolved in ethyl acetate/water mixture (1:1) (200 mL), the aqueous and organic phases separated and the organic phase extracted further with water (3 × 25 mL). The combined aqueous phases were washed with ethyl acetate (3 × 25 mL) and the aqueous layer acidified to pH 2 with 5M HCl (12.5 mL). The yellow oil which separates was extracted with ethyl acetate (3 × 50 mL), the combined extracts washed with brine (3 × 25 mL), dried over anhydrous $MgSO_4$ and concentrated by rotary evaporation to give a golden yellow oil (15.8 g, 94%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.00 (s, 1H), 6.31-6.56 (m, 4H), 3.84 (s, 3H, CH_3O), 3.84 (s, 3H, CH_3O), 3.83 (s, 3H, CH_3O), 2.04 (s, 2H) ppm.

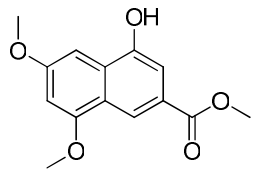
(b) Methyl 1-acetoxy-5,7-dimethoxy-3-naphthoate



The crude half ester from step (a) (15.8 g), acetic anhydride (160 mL) and sodium acetate (4.8 g, 0.058 mol) were refluxed for 4 hours under a nitrogen atmosphere. The reaction mixture was concentrated by rotary evaporation to about 1/3 of the volume and then stirred with water for 30 mins (ice cooling was required). The product was extracted with ethyl acetate (2 × 100 mL), the organic extracts washed with water and

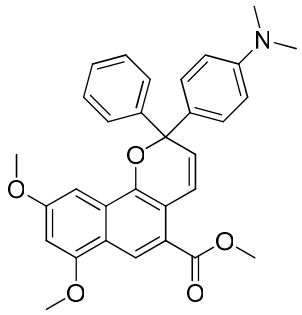
then dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation to give an orange-red solid which was slurried with MeOH and filtered to give a pale yellow solid (7.48 g). Concentration of the filtrate followed by slurrying with MeOH afforded a further 2.34 g of orange-red solid. (Total yield = 9.81 g, 57.2%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.80 (dd, *J* = 2.0 Hz, 1H), 7.80 (d, *J* = 2.0 Hz, 1H), 6.67 (d, *J* = 2.0 Hz, 1H), 6.53 (d, *J* = 2.0 Hz, 1H), 3.99 (s, 3H, CH_3O), 3.95 (s, 3H, CH_3O), 3.92 (s, 3H, CH_3O), 2.46 (s, 3H, OAc) ppm. ^{13}C NMR (200 MHz, $CDCl_3$) δ 169.2, 166.7, 161.0, 157.9, 145.4, 131.2, 124.0, 123.4, 122.3, 119.1, 98.6, 91.6, 55.7, 55.4, 52.1, 20.9 ppm.

(c) Methyl 1-hydroxy-5,7-dimethoxy-3-naphthoate



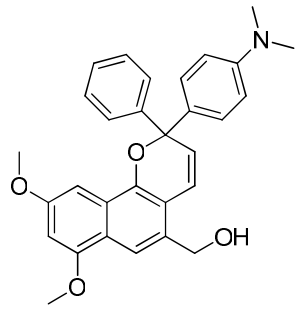
The product from step (b) (8.104 g, 0.026 mol), *p*-toluenesulfonic acid (1.3 g) and methanol (120 mL) were refluxed for 3 hours under a nitrogen atmosphere. The reaction mixture was concentrated to 1/3 of the volume and then stirred with a 1:1 mixture of ethyl acetate:water. Organic phase was separated, washed with water (3 × 20 mL), dried over anhydrous $MgSO_4$ and the solvent evaporated to yield an off-white solid (6.68 g, 96%). ^{1}H NMR (200 MHz, d_6-DMSO) δ 10.34 (s, 1H), 8.19 (dd, *J* = 2.0 Hz, 1H), 7.35 (d, *J* = 2.0 Hz, 1H), 7.03 (d, *J* = 2.0 Hz, 1H), 6.65 (d, *J* = 2.0 Hz, 1H), 3.95 (s, 3H, CH_3O), 3.87 (s, 3H, CH_3O), 3.84 (s, 3H, CH_3O) ppm. ^{13}C NMR (200 MHz, d_6-DMSO) δ 167.4 160.2, 157.7, 153.0, 129.3, 124.6, 121.6, 116.0, 99.6, 99.4, 93.5, 56.6, 55.9, 52.7 ppm.

(d) Methyl 2-(4-dimethylaminophenyl)-2-phenyl-7,9-dimethoxy-2*H*-naphtho-[1,2-*b*]pyran-5-carboxylate



A solution containing methyl 1-hydroxy-5,7-dimethoxy-3-naphthoate, step (c), (4.0 g, 0.0152 mol), 1-(4-dimethylaminophenyl)-1-phenyl-prop-2-yn-1-ol (4.21 g, 0.0168 mol) and trimethylorthoformate (3.0 g, 0.028 mol) in toluene (300 mL) was warmed to 50°C under a nitrogen atmosphere. Alumina (75 g, activated, weakly acidic, Brockmann I) was added and the mixture heated to 80°C until most of the propyn-2-yn-ol was consumed (approx. 24 hours as indicated by TLC). The cooled mixture was filtered and the alumina washed with hot toluene (2 × 100 mL). Removal of the toluene *in vacuo* gave a deep red tar, which was slurried with a small amount of diethyl ether to induced crystallisation of the product as a yellow solid in excellent purity (5.01 g, 66%). ^{1}H NMR (200 MHz, d_6-acetone) δ 8.35 (s, 1H), 7.7 (d, J = 10.0 Hz, 1H, pyran-CH), 7.53-7.58 (m, 2H), 7.17-7.37 (m, 6H), 6.62-6.67 (m, 3H), 6.41 (d, J = 10.0 Hz, 1H, pyran-CH), 4.00 (s, 3H, CH_3O-CO-), 3.96 (s, 3H, CH_3O), 3.88 (s, 3H, CH_3O), 2.87 (s, 6H, $N(CH_3)_2$) ppm.

(e) 2-(4-Dimethylaminophenyl)-2-phenyl-5-hydroxymethyl-7,9-dimethoxy-2*H*-naphtho[1,2-*b*]pyran

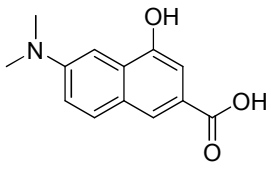


To a slurry of $LiAlH_4$ (0.73 g, 0.018 mol) in anhydrous THF (50 mL), cooled to 0°C and under nitrogen atmosphere, was slowly added a solution of methyl 2-(4-dimethylaminophenyl)-2-phenyl-7,9-dimethoxy-2*H*-naphtho-[1,2-*b*]pyran-5-

carboxylate (5.0 g, 0.01 mol) in anhydrous THF (250 mL). The mixture was stirred until no starting ester was observed by TLC (approx. 20 mins), the reaction then quenched with saturated aqueous NH_4Cl and filtered. The solvent was removed *in vacuo*, the residue extracted with CH_2Cl_2, washed with water and dried over anhydrous $MgSO_4$. The solvent was evaporated giving a blue foamy solid (4.32 g, 92%). ^{1}H NMR (200 MHz, d_6-acetone) δ 7.63 (s, 1H), 7.54-7.58 (m, 2H), 7.22-7.37 (m, 6H), 7.09 (d, J = 10.0 Hz, 1H, pyran-CH), 6.66 (d, J = 10.0 Hz, 2H), 6.55 (d, J = 2.0 Hz, 1H), 6.36 (d, J = 10.0 Hz, 1H, pyran-CH), 4.76 (s, 2H, CH_2), 3.95 (s, 3H, CH_3O), 3.92 (s, 3H, CH_3O), 2.87 (s, 6H, $N(CH_3)_2$) ppm. ^{13}C NMR (400 MHz, d_6-acetone) δ 158.3, 156.6, 150.0, 149.9, 147.0, 146.1, 132.5, 132.2, 128.7, 127.9, 127.6, 126.9, 126.4, 125.8, 121.7, 120.5, 116.0, 113.1, 111.7, 97.9, 92.3, 82.2, 62.4, 62.3, 55.1, 54.7, 39.5 ppm. MS (HR, EI): *m/z* 467.2086 ($C_{30}H_{29}NO_4$ requires 467.2091).

2,2-Bis(4-dimethylaminophenyl)-5-(2-hydroxyethoxycarbonyl)-9-dimethylamino-2*H*-naphtho[1,2-*b*]pyran. This compound is an analogue of a photochromic dye from the patent literature.[11]

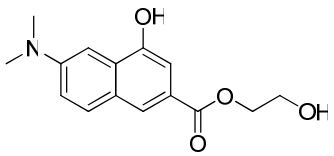
(a) 6-Dimethylamino-4-hydroxy-2-naphthoic acid



4-Dimethylaminobenzaldehyde (5.0 g, 33.5 mmol) was mixed with diethylsuccinate (6.43 g, 36.9 mmol) using a mortar and pestle until a homogeneous mixture was obtained. *t*-BuOK (4.14 g, 36.9 mmol) was then added and the mixture ground for 5-10 minutes, giving a smooth paste. The mixture was then allowed to stand at room temperature for at least 1 hour, after which it was dissolved in water and the impurities and unreacted reagents extracted with chloroform. The aqueous layer was acidified with glacial acetic acid and the mixture extracted with ethyl acetate. The extracts were combined, washed with brine, dried with $MgSO_4$, filtered and the solvent evaporated *in vacuo*. This crude product was dissolved in acetic anhydride (40

mL) together with NaOAc (2.75 g) and refluxed under nitrogen for 3 hours, after which the excess acetic anhydride and acetic acid were removed *in vacuo*. The residue was then added to a mixture of dichloromethane (30 mL) and water (20 mL), to which was added solid Na_2CO_3 until there was no further evolution of CO_2. **Caution!** The organic layer was separated, the aqueous layer extracted once more with CH_2Cl_2, the organic extracts combined, dried with $MgSO_4$ and the solvent evaporated *in vacuo*. This product was dissolved in methanol (40 mL) to which was added a solution on NaOH (5.4 g) in water (40 mL). The mixture then refluxed for 1 hour, cooled, extracted with CH_2Cl_2 to remove impurities and acidified with glacial acetic acid. The precipitated solid was collected by filtration, washed with water and then dried in a vacuum oven at approximately 50°C (3.69 g). The filtrate and washings were combined and extracted with ethyl acetate, dried with $MgSO_4$ and the solvent evaporated to give another small amount of product (0.46 g). (Total yield: 4.15 g, 54%). ^{1}H NMR(200 MHz, d_6-DMSO) δ 12.45 (s br, 1H), 10.01 (s br, 1H), 7.91 (s, 1H), 7.80 (d, J = 9.1 Hz, 1H), 7.28 (d, J = 1.4 Hz, 1H), 7.21 (dd, J = 2.6, 9.1 Hz, 1H), 7.11 (d, J = 2.6 Hz, 1H), 3.03 (s, 6H, $N(CH_3)_2$) ppm. ^{13}C NMR (50 MHz, d_6-DMSO) δ 168.0, 151.4, 149.3, 130.1, 128.6, 125.9, 123.6, 121.7, 116.5, 106.9, 99.7, 40.1 ppm. MS (EI): *m/z* 231.1 [M^+].

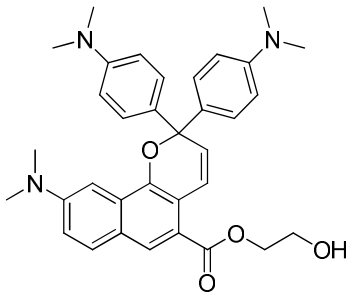
(b) (2-Hydroxyethyl) 6-dimethylamino-4-hydroxy-2-naphthoate



This compound was synthesized using the alkylation procedure of Hattori *et al.*[12] 6-Dimethylamino-4-hydroxy-2-naphthoic acid (3.85 g, 16.65 mmol) was dissolved in DMF (25 mL) to which was added $NaHCO_3$ (1.40 g, 16.65 mmol) and the mixture stirred at 100°C under nitrogen for 45 minutes. Freshly distilled and acid-free 2-bromoethanol (2.60 g, 20.8 mmol) was then added and heating continued at 100°C for approximately 2 hours (reaction monitored by TLC). The mixture was then concentrated to approximately 1/3 of the volume and then poured into water and extracted with ethyl acetate. The ethyl acetate extracts were combined and washed

with dilute aqueous $NaHCO_3$ and then brine, dried with $MgSO_4$, filtered and the solvent evaporated *in vacuo* to give the crude product (2.25 g, 49%). **Note**: The aqueous $NaHCO_3$ layer may contain unreacted starting material which can be retrieved by firstly acidifying with glacial acetic acid, (**Caution**: CO_2 evolved) and the precipitated solid collected by filtration, washed with water and dried in a vacuum oven. ^{1}H NMR (200 MHz, d_6-acetone) δ 8.03 (s, 1H), 7.82 (d, J = 10 Hz, 1H), 7.38 (d, J = 1.5 Hz, 1H), 7.28 (m, 2H), 4.36 (m, 2H), 3.88 (m, 2H), 3.11 (s, 6H, $N(CH_3)_2$) ppm.

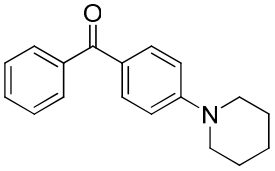
(c) 2,2-Bis(4-dimethylaminophenyl)-5-(2-hydroxyethoxycarbonyl)-9-dimethylamino-2*H*-naphtho[1,2-*b*]pyran



A stirred suspension of (2-hydroxyethyl) 6-dimethylamino-4-hydroxy-2-naphthoate (0.70 g, 2.54 mmol), 1,1-bis(4-dimethylaminophenyl)prop-2-yn-1-ol[1] (0.83 g, 2.80 mmol) and alumina (activated, weakly acidic, Brockman I) (5.0 g) in toluene (50 mL) was heated to reflux using a Dean-Stark apparatus under nitrogen for one hour. The cooled mixture was filtered through a small plug of silica, eluting further with ethyl acetate. Removal of the solvent gave a deep blue residue of the crude product which was purified by column chromatography, eluting with 0-10% MeOH/$CHCl_3$ to afford the product (0.450 g) of approximate 80% purity by ^{1}H NMR. The compound was re-purified by preparative HPLC giving the pure product (0.30 g, 22%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.63 (d, J = 9.1 Hz, 1H), 7.61 (d, J = 10.1 Hz, 1H), 7.42-7.35 (m, 5H), 7.10 (dd, J = 2.6, 9.1Hz, 1H), 6.68-6.60 (m, 4H), 6.14 (d, 1H, J = 10.1 Hz), 4.47-4.42 (m, 2H), 4.02-3.92 (m, 2H), 3.09 (s, 6H), 2.93 (s, 12H) ppm. MS (HR, EI): *m/z* 551.2775 ($C_{34}H_{37}N_3O_4$ requires 551.2779).

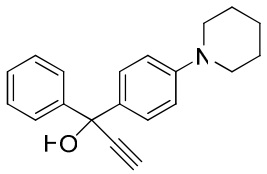
2-Phenyl-2-(4-piperidinophenyl)-5-(2-hydroxyethoxycarbonyl)-9-dimethylamino -2*H*-naphtho[1,2-*b*]pyran. This compound is an analogue of a photochromic dye from the patent literature.[11]

(a) 4-Piperidinobenzophenone



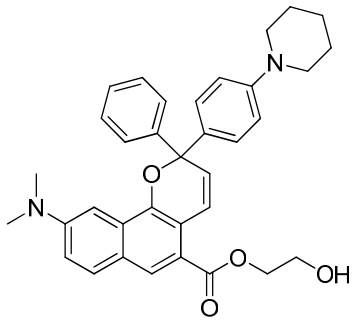
4-Flourobenzophenone (4.0 g, 20.0 mmol) and piperidine (5.1 g, 60.0 mmol) were dissolved in acetonitrile (7 mL). The mixture was heated in a microwave reactor at 200°C for one hour. The mixture was cooled, the solvent removed *in vacuo* and the residue purified by column chromatography (silica gel, 50% petroleum ether/CH_2Cl_2 → 100% CH_2Cl_2) to afford the desired product as a pale yellow solid (3.1 g, 58%). ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.82-7.71 (m, 4H), 7.58-7.41 (m, 3H), 6.91(d br, *J* = 8.5 Hz, 2H), 3.39 (m, 4H), 1.68 (m br, 6H) ppm.

(b) 1-Phenyl-1-(4-piperidinophenyl)-prop-2-yn-1-ol



This compound was synthesized from 4-piperidinobenzophenone using the procedure of Gabbutt *et al.*[1] ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.60 (m, 2H), 7.44 (d, *J* = 8.8 Hz, 2H), 7.38-7.27 (m, 3H), 6.88 (d, *J* = 8.8 Hz, 2H), 3.16 (m, 4H), 2.75 (s br, 1H), 1.75-1.50 (m br, 6H) ppm.

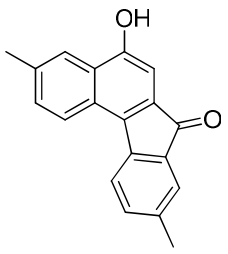
(c) 2-Phenyl-2-(4-piperidinophenyl)-5-(2-hydroxyethoxycarbonyl)-9-dimethylamino-2*H*-naphtho[1,2-*b*]pyran



(2-Hydroxyethyl) 6-dimethylamino-4-hydroxy-2-naphthoate (1.7 g, 6.18 mmol), 1-phenyl-1-(4-piperidinophenyl)prop-2-yn-1-ol (1.80 g, 6.18 mmol) and alumina (activated, weakly acidic, Brockman I) (5 g) in toluene (50 mL) was heated to reflux for 5 hours. The reaction mixture was filtered and the solvent evaporated *in vacuo*. The residue was purified by column chromatography (silica gel, CH_2Cl_2 → 1% MeOH/CH_2Cl_2) giving the product having a persistent impurity. The pure product was obtained after purification by preparative HPLC (0.35 g, 10%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.66 (m, 2H), 7.52 (m, 2H), 7.37-7.20 (m, 6H), 7.12 (dd, *J* = 2.5, 9.1 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.17 (d, *J* = 10.1 Hz, 1H, pyran-CH), 4.46 (m, 2H), 3.98 (m, 2H), 3.12 (m, 10H), 1.65 (m, 3H), 1.54 (m, 3H) ppm.

3,3-Bis(4-methoxyphenyl)-6,11,13-trimethyl-13-(2-hydroxyethoxy)-indeno[2,1-*f*]naphtho[1,2-*b*]pyran. This compound was synthesized using the patent procedure[13] with alterations to a number of the synthesis steps.

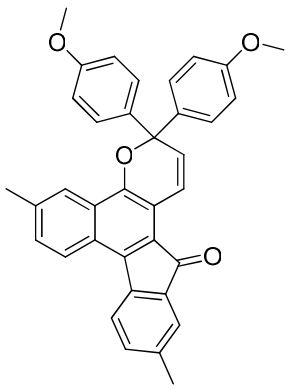
(a) 3,9-Dimethyl-5-hydroxy-7*H*-benzo[C]-fluoren-7-one



This compound was synthesized using the Friedel-Crafts cyclization procedure of Aki *et al.*[14] 1-(4-Methylphenyl)-4-hydroxy-6-methyl-2-naphthoic acid[13] (4.0 g, 13.68 mmol) was ground into a fine powder with a mortar and pestle and then added in

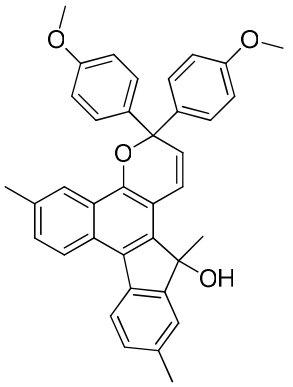
small portions over 5 minutes to methanesulfonic acid (60 mL) at 60°C. After 2 hours the thick mixture was added to water and the solid product collected by filtration, washed with water and dried overnight in a vacuum oven at 50°C. The compound was further purified by stirring in petroleum ether for 15 minutes, filtering and drying in air (3.5 g, 93%). ^{1}H NMR (400 MHz, d_6-acetone) δ 9.62 (s br, 1H), 8.44 (d, J = 8.6 Hz, 1H), 8.12 (s, 1H), 7.93 (d, J = 7.5 Hz, 1H), 7.55 (dd, J = 1.4, 8.6 Hz, 1H), 7.35 (m, 2H), 7.08 (s, 1H), 2.55 (s, 3H), 2.36 (s, 3H) ppm.

(b) 3,3-Bis(4-methoxyphenyl)-6,11-dimethyl-13-oxo-indeno[2,1-*f*]naphtho[1,2-*b*]pyran



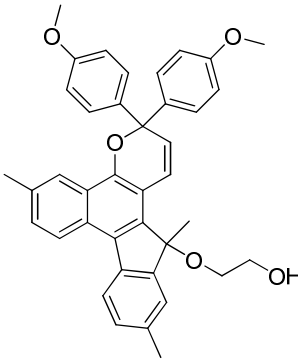
This compound was synthesized using the procedure of Zhao and Carreira[15] from 3,9-dimethyl-5-hydroxy-7*H*-benzo[C]-fluoren-7-one and 1,1-bis(4-methoxyphenyl)prop-2-yn-1-ol.[1] ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.21 (d, J = 8.7 Hz, 1H), 8.08 (s, 1H), 7.84 (d, J = 10 Hz, 1H), 7.69 (d, J = 7.6 Hz, 1H), 7.44-7.33 (m, 6H), 7.20 (d, J = 7.6 Hz, 1H), 6.85 (m, 4H), 6.27 (d, J = 10 Hz, 1H), 3.77 (s, 6H), 2.52 (s, 3H), 2.34 (s, 3H) ppm.

(c) 3,3-Bis(4-methoxyphenyl)-6,11,13-trimethyl-13-hydroxy-indeno[2,1-*f*]naphtho[1,2-*b*]pyran



This compound was synthesized using the patent procedure of Walters and van Gemert,[13] which involved the reaction of 3,3-bis(4-methoxyphenyl)-6,11-dimethyl-13-oxo-indeno[2,1-*f*]naphtho[1,2-*b*]pyran with MeMgCl in anhydrous THF.

(d) 3,3-Bis(4-methoxyphenyl)-6,11,13-trimethyl-13-(2-hydroxyethoxy)-indeno[2,1-*f*]naphtho[1,2-*b*]pyran

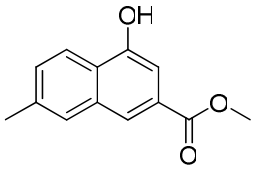


3,3-Bis(4-methoxyphenyl)-6,11,13-trimethyl-13-(2-hydroxyethoxy)-indeno[2,1-*f*]naphtho[1,2-*b*]pyran[13] (0.50 g, 0.092 mmol), dry ethylene glycol (2.4g) and pyridinium *p*-toluenesulfonic acid (0.030 g) were dissolved in acetonitrile (15 mL) and heated in a microwave reactor at 120°C for 15 minutes. The mixture was cooled and the solvent removed *in vacuo*. The residue was dissolved in ethyl acetate and the solution filtered through a small plug of silica gel. The ethyl acetate was evaporated *in vacuo* and the crude product purified by chromatography using a chromatotron (silica gel, 100% CH_2Cl_2 → 2% MeOH/CH_2Cl_2) giving the desired product as a dark purple/black solid (0.38 g, 70%). ^{1}H NMR (400 MHz, d_6-acetone) δ 8.52 (d, J = 8.7 Hz, 1H), 8.25 (s, 1H), 8.05 (d, J = 7.9 Hz, 1H), 7.55-7.45 (m, 6H), 7.35 (s, 1H), 7.24

(d, *J* = 7.9 Hz, 1H), 6.89 (m, 4H), 6.37 (d, *J* = 9.9 Hz, 1H), 3.77 (s, 3H), 3.72 (s, 3H), 3.53 (m, 2H), 2.91 (t, *J* = 5.2 Hz, 2H), 2.55 (s, 3H), 2.41 (s, 3H), 1.69 (s, 3H) ppm.

2,2-Diphenyl-5-(carboxylic acid)-8-methyl-2*H*-naphtho[1,2-*b*]pyran. This compound was synthesized using a modified patent procedure.[13]

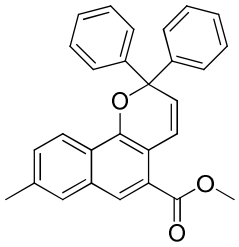
(a) Methyl 4-hydroxy-7-methyl-2-naphthoate



m-Tolualdehyde (5.0 g, 41.6 mmol), dimethylsuccinate (6.69 g, 45.8 mmol) and *t*-BuOK (5.14 g, 45.8 mmol) were combined and ground using a mortar and pestle for 5 minutes. The resulting sticky brown paste was left to stand at RT for 3 hours. The mixture was treated with water and extracted with CH_2Cl_2 (an emulsion forms which was broken with the addition of brine). The aqueous layer was acidified with 1M HCl and extracted with diethyl ether. The ether extracts were combined, washed with water then brine and dried with $MgSO_4$. The solvent was evaporated *in vacuo* leaving the crude product (8.47 g) which was then dissolved in acetic anhydride (30 mL) and NaOAc (0.25 g) added. This mixture was refluxed under nitrogen for 2 hours after which the excess reagent and acetic acid was removed *in vacuo*. Water was added to the residue and solid Na_2CO_3 added until the evolution of CO_2 ceased. The CH_2Cl_2 layer was washed with water and brine, dried with $MgSO_4$, filtered and the solvent evaporated. The crude residue then dissolved in MeOH (40 mL) together with *p*-toluenesulfonic acid (0.5 g) and refluxed under nitrogen for 1 hour. The solvent was evaporated *in vacuo* and residue dissolved in diethyl ether which was then washed with aqueous $NaHCO_3$ and brine, dried with $MgSO_4$ and filtered through a small plug of silica gel. The solvent was evaporated giving an oily product which contained some solid. This material is a mixture of the two possible regioisomers, methyl 4-hydroxy-5-methyl-2-naphthoate and methyl 4-hydroxy-7-methyl-2-naphthoate. The latter, correct regioisomer was selectively crystallised from the mixture by trituration with a

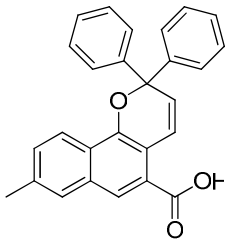
small amount of diethyl ether/hexane (1:1) and cooling in a refrigerator for a few hours. The solid was collected by filtration and washed with a small amount of diethyl ether/hexane (1:1) (0.79 g, 9%). ^{1}H NMR (400 MHz, d_6-acetone) δ 9.25 (s, 1H, OH), 8.17 (d, J = 8.6 Hz, 1H), 8.04 (s, 1H), 7.77 (s, 1H), 7.45 (dd, J = 1.6, 8.6 Hz, 1H), 7.41 (d, J = 1.6 Hz, 1H), 3.90 (s, 3H, CH_3O), 2.51 (s, 3H, $ArCH_3$) ppm. ^{13}C NMR (50 MHz, d_6-acetone) δ 168.5, 155.2, 138.7, 136.2, 131.2, 129.9, 129.8, 127.3, 123.9, 123.3, 108.0, 53.3, 22.6 ppm. MS (EI): *m/z* 216.1 [M^+].

(b) 2,2-Diphenyl-5-methoxycarbonyl-8-methyl-2*H*-naphtho[1,2-*b*]pyran



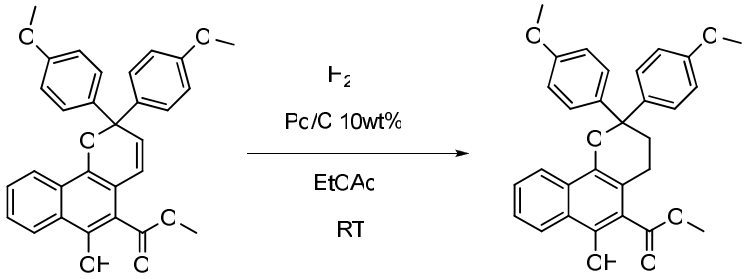
This compound was synthesized using the procedure of Zhao and Carreira.[15] Methyl 4-hydroxy-7-methyl-2-naphthoate (1.056 g, 4.88 mmol), 1,1-diphenyl-2-propyn-1-ol (1.017 g, 4.88 mmol), pyridinium *p*-toluenesulfonate (0.06 g, 0.023 mmol) and trimethylorthoformate (2.07 g, 19.5 mmol) were combined in 1,2-dichloroethane (25 mL) and refluxed under nitrogen for 2 hours. The reaction mixture was passed through a short column of basic alumina eluting with chloroform to remove unreacted naphthol. The solvent was evaporated and the resulting oil triturated with a small amount of diethyl ether, inducing crystallization of the product as a pale orange crystalline solid, which was collected by filtration and washed with diethyl ether/hexane (1:1), (0.747 g, 38%). ^{1}H NMR (400 MHz, d_6-acetone) δ 8.51 (d, J = 8.6 Hz, 1H), 8.01 (s, 1H), 7.70 (s, 1H), 7.67 (d, J = 10.1 Hz, 1H), 7.59 (m, 4H), 7.53 (dd, J = 1.5, 8.6 Hz, 1H), 7.34 (m, 4H), 7.25 (m, 2H), 6.48 (d, J = 10.1 Hz, 1H), 3.91 (s, 3H, CH_3O) 2.50 (s, 3H, $ArCH_3$) ppm. MS (EI): *m/z* 406.1 [M^+].

(c) 2,2-Diphenyl-5-carboxylic acid-8-methyl-2*H*-naphtho[1,2-*b*]pyran



2,2-Diphenyl-5-methoxycarbonyl-8-methyl-2*H*-naphtho[1,2-*b*]pyran (0.747 g, 1.84 mmol) was dissolved in THF (25 mL) and a solution of NaOH (0.38 g) in water (15 mL) and ethanol (10 mL) added. The mixture was stirred at 75°C for 2 hours, pured into 0.5M HCl (100 mL) added and extracted with ethyl acetate. The organic extracts were combined, washed with dilute HCl and brine, dried with $MgSO_4$ and the solvent evaporated. The crude product was recrystallized from hot EtOH giving the pure product as a pale orange solid (0.515 g, 71%). ^{1}H NMR (400 MHz, d_6-acetone) δ 8.37 (d, *J* = 8.6 Hz, 1H), 8.11 (s, 1H), 7.78 (d, *J* = 10.1 Hz, 1H), 7.72 (s, 1H), 7.59 (m, 4H), 7.54 (dd, *J* = 1.5, 8.6 Hz, 1H), 7.35-7.32 (m, 4H), 7.26 (m, 2H), 6.46 (d, *J* = 10.1 Hz, 1H), 2.51 (s, 3H, $ArCH_3$) ppm. MS (EI): *m/z* 392.1 [M^+].

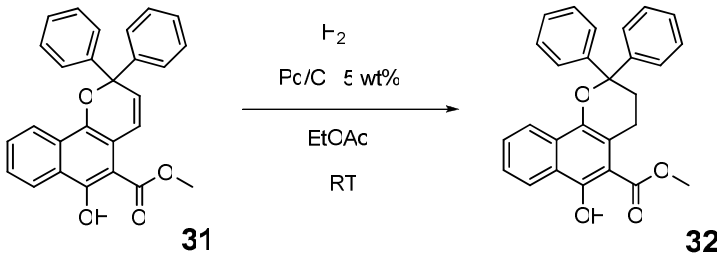
2,2-Bis(4-methoxyphenyl)-5-methoxycarbonyl-6-hydroxy-3,4-dihydro-2*H*-naphtho[1,2-b]pyran.



2,2-Bis(4-methoxyphenyl)-5-methoxycarbonyl-6-hydroxy-2*H*-naphtho[1,2-b]pyran[16] (1.008 g, 2.15 mmol) was dissolved in ethyl acetate (50 mL) and Pd/C (5 wt%) (0.10 g) was then added. Hydrogen was slowly bubbled through the mixture, with stirring, for 19 hours. (Note: 10 wt% Pd/C can also be used. A larger amount of catalyst decreases the reaction time. The reaction can be stopped once TLC analysis shows no more photochromic material). The mixture was filtered through a small plug

of silica gel (or Celite) and the solvent evaporated *in vacuo*. The residue was then treated with a small amount of diethyl ether causing spontaneous crystallisation of the product as a yellow solid (0.826 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.28 (s, 1H), 8.42 (m, 2H), 7.69 (m, 1H), 7.55 (m, 1H), 7.40 (m, *J* = 8.9 Hz, 4H), 6.83 (m, *J* = 8.9 Hz, 4H), 3.91 (s, 3H, $COOCH_3$), 3.76 (s, 6H, $ArOCH_3$), 2.99 (t, *J* = 6.6 Hz, 2H), 2.64 (t, *J* = 6.6 Hz, 2H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$) δ 172.8, 158.5, 156.8, 141.4, 137.2, 129.2, 127.1, 125.8, 124.4, 124.0, 121.4, 113.7, 113.1, 105.0, 80.2, 55.2, 52.0, 32.4, 23.8 ppm. MS (EI): *m/z* 470.2 [M^+].

2,2-Diphenyl-5-methoxycarbonyl-6-hydroxy-3,4-dihydro-2*H*-naphtho[1,2-b]pyran, 32.

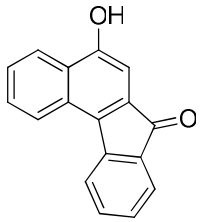


31 32

2,2-Diphenyl-5-methoxycarbonyl-6-hydroxy-2*H*-naphtho[1,2-b]pyran[16] (1.50 g, 3.67 mmol) was dissolved in ethyl acetate (50 mL) and Pd/C (5 wt%) (0.75 g) was then added. Hydrogen was slowly bubbled through the mixture until TLC indicated complete conversion (*ca.* 2.5 hours). The mixture was filtered through a small plug of silica gel and the solvent evaporated *in vacuo*. The crystalline product was washed with a small amount of diethyl ether/hexane (1:1) giving the pure product (1.30 g, 86%). ^{1}H NMR (400 MHz, d_6-acetone) δ 12.23 (s, 1H, OH), 8.55 (d, *J* = 8.4 Hz, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 7.81 (m, 1H), 7.63 (m, 5H), 7.32 (m, 4H), 7.22 (m, 2H), 3.93 (s, 3H, OCH_3), 3.06 (t, *J* = 6.6 Hz, 2H, dihydropyran-CH_2), 2.82 (m, overlap with H_2O and HDO peaks, 2H, dihydropyran-CH_2) ppm.

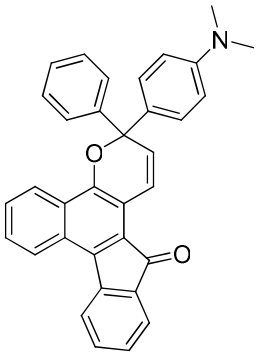
3-(4-Dimethylaminophenyl)-3-phenyl-13-methyl-13-(2-hydroxyethoxy)-indeno[2,1-*f*]naphtho[1,2-*b*]pyran.

(a) 5-Hydroxy-7*H*-benzo[C]-fluoren-7-one



This compound was synthesized using the procedure of Aki *et al.*[14] from 1-phenyl-4-hydroxy-2-naphthoic acid.[13] 1-Phenyl-4-hydroxy-2-naphthoic acid (2.00 g, 7.57 mmol) was added in portions, with stirring, to methanesulfonic acid (15 mL) at 60°C. The mixture was stirred for an additional 1.5 hours after which it was slowly poured into ice water. The purple solid was collected by filtration, thoroughly washed with water and dried in a vacuum oven at 50°C overnight, giving the product with excellent purity (1.70 g, 91%). ^{1}H NMR (200 MHz, d_6-acetone) δ 9.74 (br, 1H, OH), 8.59 (m, 1H), 8.37 (m, 1H), 8.11 (d, J = 8.1 Hz, 1H), 7.52-7.77 (m, 4H), 7.28 (t, J = 7.4 Hz, 1H), 7.15 (s, 1H) ppm. ^{13}C NMR (50 MHz, d_6-DMSO) δ 193.9, 155.2, 145.0, 135.1, 133.5, 132.4, 132.1, 129.2, 128.5, 128.1, 127.3, 127.1, 124.6, 123.6, 123.3, 122.3, 101.5 ppm. MS (ESI): *m/z* 245.4 $[M-H]^-$.

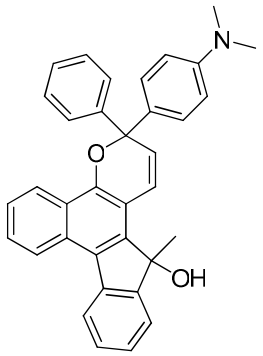
(b) 3-(4-Dimethylaminophenyl)-3-phenyl-13-oxo-indeno[2,1-*f*]naphtho[1,2-*b*]pyran



This compound was synthesized as described in Step (d) of the synthesis of 2-(4-Dimethylaminophenyl)-2-phenyl-5-hydroxymethyl-7,9-dimethoxy-2*H*-naphtho[1,2-*b*]pyran, using 5-Hydroxy-7*H*-benzo[C]-fluoren-7-one and 1-(4-

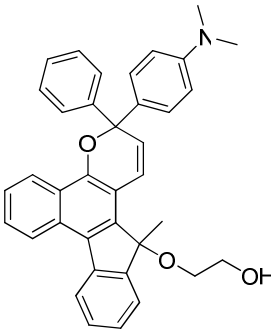
Dimethylaminophenyl)-1-phenyl-prop-2-yn-1-ol. Reflux time was 10 minutes and the pure product obtained after column chromatography (silica gel, EtOAc/hexane, 1:2).

(c) 3-(4-Dimethylaminophenyl)-3-phenyl-13-hydroxy-13-methyl-indeno[2,1-*f*]naphtho[1,2-*b*]pyran



This compound was synthesized using the patent procedure of Walters and van Gemert,[13] which involved the reaction of 3-(4-Dimethylaminophenyl)-3-phenyl-13-oxo-indeno[2,1-*f*]naphtho[1,2-*b*]pyran with MeMgCl in anhydrous THF.

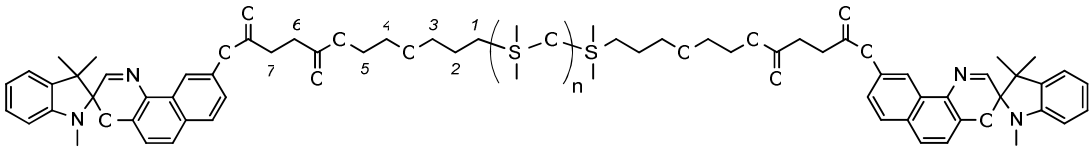
(d) 3-(4-Dimethylaminophenyl)-3-phenyl-13-(2-hydroxyethoxy)-13-methyl-indeno[2,1-*f*]naphtho[1,2-*b*]pyran



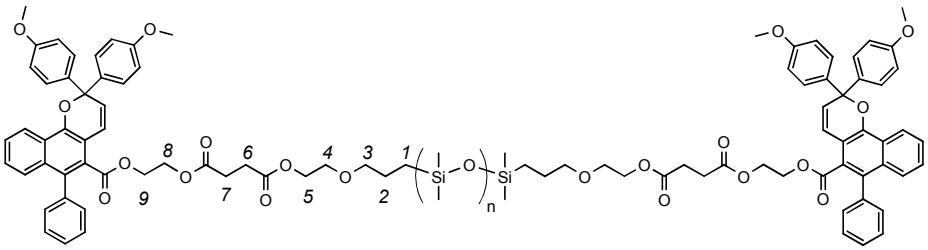
This compound was synthesized as outlined in Step (d) of the synthesis of 3,3-Bis(4-methoxyphenyl)-6,11,13-trimethyl-13-(2-hydroxyethoxy)-indeno[2,1-*f*]naphtho[1,2-*b*]pyran, using 3-(4-Dimethylaminophenyl)-3-phenyl-13-hydroxy-13-methyl-indeno[2,1-*f*]naphtho[1,2-*b*]pyran. Microwave heating was conducted at 125°C for 4 hours followed by another 3 hours at 140°C. The pure

material was obtained after column chromatography (silica gel, EtOAc/hexane, 1:1). ^{1}H NMR (400 MHz, d_6-acetone) δ 8.66 (d, J = 8.4 Hz, 1H), 8.50 (d, J = 8.4 Hz, 1H), 8.21 (d, J = 7.8 Hz, 1H), 7.66-7.54 (m, 6H), 7.45-7.21 (m, 7H), 6.68 (d, J = 8.9 Hz, 1H), 6.62 (d, J = 8.9 Hz, 1H), 6.44-6.37 (2 × d, J = 9.9 Hz, 1H, pyran-CH), 3.55 (m, 2H, CH_2OH), 2.93 (m, 2H, CH_2O), 2.87 (s, 3H, CH_3N), 2.83 (s, 3H, CH_3N), 1.74 and 1.71 (2 × s, 3H, indeno-CH_3) ppm.

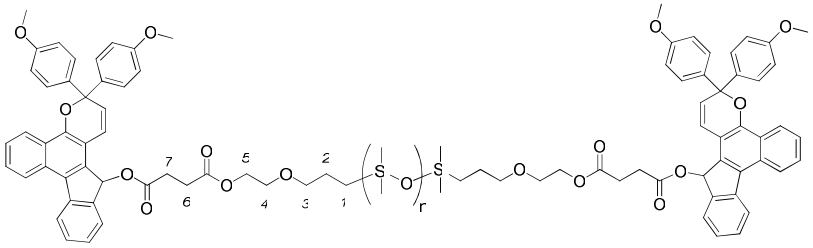
Telechelic Photochromic Dye-Poly(Dimethylsiloxane) Conjugates



Telechelic poly(dimethylsiloxane) conjugated 9'-Hydroxy-1,3,3-trimethylspiro[indoline-2,3'-[3*H*]-naphtho[2,1-*b*][1,4]oxazine], 7. This conjugate was synthesized using *Method B*. The pure conjugate was obtained as a green tar. A sample of the material was fractionated by column chromatography (silica gel, diethyl ether/hexane, 2:3) and average molecular weights determined by ^{1}H NMR analysis. Nonfractionated product, **7**: M_n = 2,123 (n_{PDMS} = 13.6). Fraction 1, **7a**: M_n = 2,830 (n_{PDMS} = 23.1). Fraction 2, **7b**: M_n = 1,592 (n_{PDMS} = 6.4). ^{1}H NMR (400 MHz, d_6-acetone) δ 8.26 (d, J = 2.0 Hz, 2H), 7.87 (d, J = 8.8 Hz, 2H), 7.82 (s overlapping, 2H), 7.80 (d overlapping, 2H), 7.21-7.13 (m, 6H), 7.03 (d, J = 8.9 Hz, 2H), 6.87 (t, J = 7.4 Hz, 2H), 6.65 (d, J = 7.7 Hz, 2H), 4.25 (t, J = 4.8 Hz, 4H, CH_2-5), 3.65 (t, J = 4.8 Hz, 4H, CH_2-4), 3.44 (t, J = 6.7 Hz, 4H, CH_2-3), 2.99 (t, J = 6.6 Hz, 4H, CH_2-7), 2.81 (t overlapping, J = 6.6 Hz, 4H, CH_2-6), 2.77 (s overlapping, 6H, NCH_3), 1.62 (m, 4H, CH_2-2), 1.34 (2 x s overlapping, 12H, geminal-CH_3 spirooxazine), 0.59 (m, 4H, CH_2-1), 0.13-0.09 (m, $SiCH_3$) ppm.

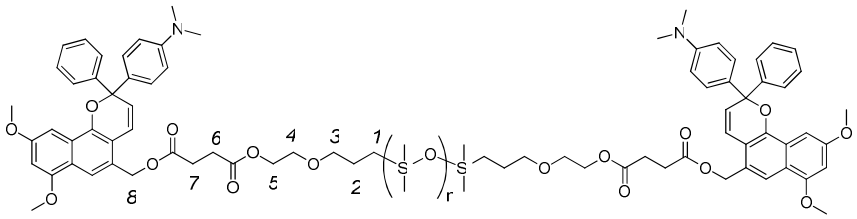


Telechelic poly(dimethylsiloxane) conjugated 2,2-Bis(4-methoxyphenyl)-5-(2-hydroxyethoxycarbonyl)-6-phenyl-[2*H*]-naphtho[1,2-*b*]pyran, 10. This conjugate was synthesized using *Method B* and purified by column chromatography (silica gel, diethyl ether/hexane, 5:1), giving the product as a pink tar. A sample of the material was fractionated by column chromatography (silica gel, diethyl ether/hexane, 2:1) and average molecular weights determined by ^{1}H NMR analysis. Nonfractionated product, **10**: M_n = 2,592 (n_{PDMS} = 14.1). Fraction 1, **10a**: M_n = 3,443 (n_{PDMS} = 25.6). Fraction 2, **10b**: M_n = 2,749 (n_{PDMS} = 16.2). Fraction 3, **10c**: M_n = 2,447 (n_{PDMS} = 12.2). Fraction 4, **10d**: M_n = 2,100 (n_{PDMS} = 7.5). ^{1}H NMR (400 MHz, d_6-acetone) δ 8.46 (d, *J* = 8.4 Hz, 2H), 7.61 (m, 2H), 7.50-7.44 (m, 18H), 7.32 (m, 4H), 6.91 (d, *J* = 8.7 Hz, 8H), 6.85 (d, *J* = 10.0 Hz, 2H, pyran-CH), 6.45 (d, *J* = 10.0 Hz, 2H, pyran-CH), 4.19 (t, *J* = 4.6 Hz, 4H, CH_2-8), 4.13 (t, *J* = 4.9 Hz, 4H, CH_2-5), 3.99 (t, *J* = 4.6 Hz, 4H, CH_2-9), 3.76 (s, 12H, CH_3OAr), 3.54 (t, *J* = 4.9 Hz, 4H, CH_2-4), 3.37 (t, *J* = 6.8 Hz, 4H, CH_2-3), 2.61 (s, 8H, CH_2-6,7), 1.59 (m, 4H, CH_2-2), 0.58 (m, 4H, CH_2-1), 0.13-0.09 (m, $SiCH_3$) ppm.

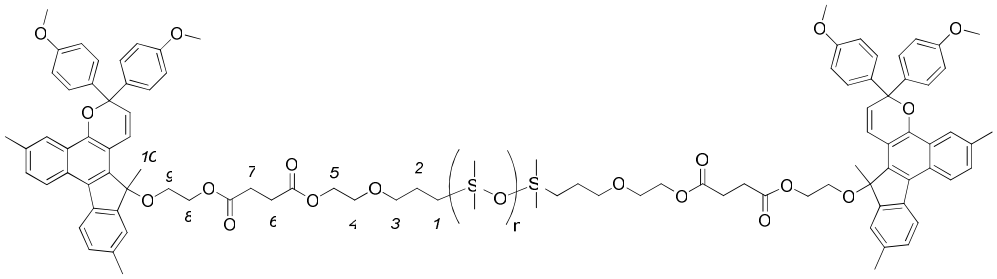


Telechelic poly(dimethylsiloxane) conjugated 3,3-Bis(4-methoxyphenyl)-13-hydroxy-indeno[2,1-*f*]naphtho[1,2-*b*]pyran, 13. This conjugate was synthesized using *Method B*. A sample of the material was fractionated by column chromatography (silica gel, CH_2Cl_2→1%MeOH/CH_2Cl_2) and average molecular weights determined by ^{1}H NMR analysis. Nonfractionated product, **13**: M_n = 2,417 (n_{PDMS} = 13.4). Fraction 1, **13a**: M_n = 3,236 (n_{PDMS} = 24.4). Fraction 2, **13b**: M_n =

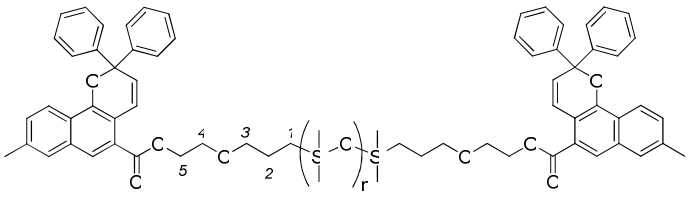
2,465 (n_{PDMS} = 14.0). Fraction 3, **13c**: M_n = 2,269 (n_{PDMS} = 11.4). Fraction 4, **13d**: M_n = 2,101 (n_{PDMS} = 9.1). Fraction 5, **13e**: M_n = 2,048 (n_{PDMS} = 8.4). ^{1}H NMR (400 MHz, d_6-acetone) δ 8.67 (d, *J* = 6.6 Hz, 2H), 8.48 (d, *J* = 8.4 Hz, 2H), 8.23 (d, *J* = 5.9 Hz, 2H), 7.69-7.56 (m, 6H), 7.51-7.45 (m, 10H), 7.28-7.24, (m, 2H), 7.06 (m, 2H), 6.96 (d, *J* = 10 Hz, 2H, pyram-CH), 6.88 (m, 8H), 6.42 (d, *J* = 10 Hz, 2H, pyran-CH), 4.23- 4.21 (t, *J* = 4.7 Hz, 4H, CH_2-5), 3.74 (d, *J* = 6.6 Hz, 12H, OCH_3), 3.60 (m, 4H, CH_2-4), 3.39 (t, *J* = 6.6 Hz, 4H, CH_2-3), 2.77-2.72 (m, 8H, CH_2-6,7), 1.62-1.55 (m, 4H, CH_2-2), 0.58-0.54 (m, 4H, CH_2-1), 0.12-0.07 (m, $SiCH_3$) ppm.



Telechelic poly(dimethylsiloxane) conjugated 2-(4-Dimethylaminophenyl)-2-phenyl-5-hydroxymethyl-7,9-methoxy-[2*H*]-naphtho[1,2-*b*]pyran, 16. This conjugate was synthesized using *Method B*. The crude product was purified by column chromatography (silica gel, ethyl acetate/hexane, 1:1) giving the product as a purple/blue tar. A sample of the material was fractionated by column chromatography (silica gel, diethyl ether/hexane, 4:1). Average molecular weights were determined by ^{1}H NMR analysis. Nonfractionated product, **16**: M_n = 2,402 (n_{PDMS} = 14.0). Fraction 1, **16a**: M_n = 2,908 (n_{PDMS} = 20.8). Fraction 2, **16b**: M_n = 2,293 (n_{PDMS} = 12.5). Fraction 3, **16c**: M_n = 1,996 (n_{PDMS} = 8.5). ^{1}H NMR (200 MHz, d_6-acetone) δ 7.66 (s, 2H), 7.57 (m, 4H), 7.38-7.31 (m, 8H), 7.27-7.22 (m, 4H), 6.98 (d, *J* = 9.9 Hz, 2H, pyran-CH), 6.65 (m, 4H), 6.58 (d, *J* = 2.2 Hz, 2H), 6.39 (d, *J* = 10 Hz, 2H, pyran-CH), 5.28 (s, 4H, $ArCH_2O$), 4.17 (m, 4H, CH_2-5), 3.96 (s, 6H, OCH_3), 3.93 (s, 6H, OCH_3), 3.56 (m, 4H, CH_2-4), 3.39 (t, *J* = 6.8 Hz, 4H, CH_2-3), 2.87 (s, 12H, $N(CH_3)_2$), 2.64 (s, 8H, CH_2-6,7), 1.60 (m, 4H, CH_2-2), 0.58 (m, 4H, CH_2-1), 0.13-0.08 (m, $SiCH_3$) ppm.

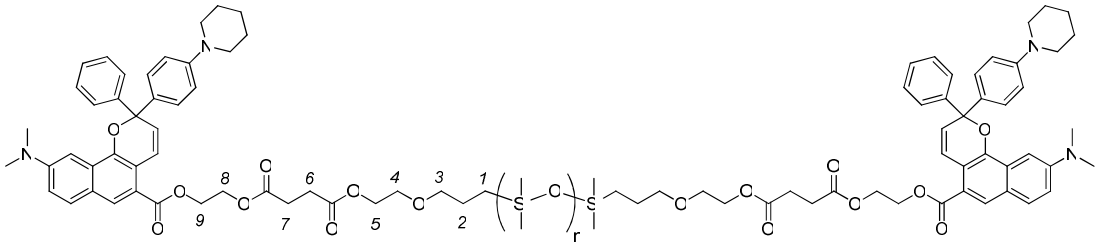


Telechelic poly(dimethylsiloxane) conjugated 3,3-Bis(4-methoxyphenyl)-6,11,13-trimethyl-13-hydroxy-indeno[2,1-*f*]naphtho[1,2-*b*]pyran, 19. This conjugate was synthesized using *Method A*. The conjugate was obtained after purification using a chromatotron, eluting with 2% MeOH/CH_2Cl_2. A sample of the material was fractionated also on a chromatotron, eluting with 15% ethyl acetate/petroleum ether. Average molecular weights were determined by ^{1}H NMR analysis. Nonfractionated product, **19**: M_n = 2,588 (n_{PDMS} = 13.4). Fraction 1, **19a**: M_n = 2,924 (n_{PDMS} = 17.9). Fraction 2, **19b**: M_n = 2,615 (n_{PDMS} = 13.7). Fraction 3, **19c**: M_n = 2,249 (n_{PDMS} = 8.8). Fraction 4, **19d**: M_n = 2,045 (n_{PDMS} = 6.0). ^{1}H NMR (400 MHz, d_6-acetone) δ 8.51 (d, *J* = 8.7 Hz, 2H), 8.24 (s, 2H), 8.06 (d, *J* = 7.9 Hz, 2H), 7.53-7.45 (m, 12H), 7.36 (s, 2H), 7.25 (d, *J* = 7.8 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 4H), 6.85 (d, *J* = 8.7 Hz, 4H), 6.42 (d, *J* = 9.9 Hz, 2H, pyran-CH), 4.14 (m, 4H, CH_2-5), 4.08 (t, *J* = 4.8 Hz, 4H, CH_2-8), 3.78 (s, 6H), 3.72 (s, 6H), 3.56 (m, 4H, CH_2-4), 3.39 (t, *J* = 6.8 Hz, 4H, CH_2-3), 3.03 (m, 4H, CH_2-9), 2.60 (m, 8H, CH_2-6,7), 2.55 (s, 6H, $ArCH_3$), 2.42 (s, 6H, $ArCH_3$), 1.70 (s, 6H, CH_3-10), 1.59 (m, 4H, CH_2-2), 0.58 (m, 4H, CH_2-1), 0.12-0.08 (m, $SiCH_3$) ppm.

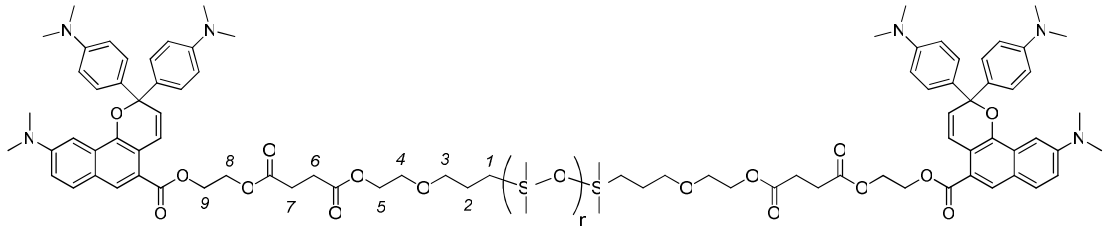


Telechelic poly(dimethylsiloxane) conjugated 2,2-Diphenyl-5-carboxylic acid-8-methyl-2*H*-naphtho[1,2-*b*]pyran, 22. This conjugate was synthesized from 2,2-Diphenyl-5-carboxylic acid-8-methyl-2*H*-naphtho[1,2-*b*]pyran and hydroxyl-terminated PDMS (Gelest Inc., DMS-C15) using *Method A*. The product was obtained

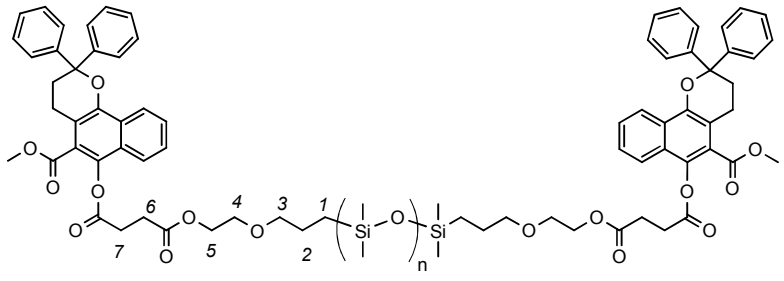
after filtration of the reaction mixture through a short plug of silica gel, eluting with CH_2Cl_2. A portion of the material was then fractionated by column chromatography (silica gel, diethyl ether/hexane, 1:2). Average molecular weights were determined by ^{1}H NMR analysis. Nonfractionated product, **22**: M_n = 1,960 (n_{PDMS} = 12.8). Fraction 1, **22a**: M_n = 2,969 (n_{PDMS} = 26.4). Fraction 2, **22b**: M_n = 2,034 (n_{PDMS} = 13.8). Fraction 3, **22c**: M_n = 1,632 (n_{PDMS} = 8.3). Fraction 4, **22d**: M_n = 1,465 (n_{PDMS} = 6.1). ^{1}H NMR (400 MHz, *d*$_6$-acetone) δ 8.36 (d, *J* = 8.6 Hz, 2H), 8.02 (s, 2H), 7.71 (d, *J* = 10.1 Hz, 2H, pyran-CH), 7.64 (s, 2H), 7.59 (m, 8H), 7.51 (dd, *J* = 8.6, 1.4 Hz, 2H), 7.33 (m, 8H), 7.24 (m, 4H), 6.43 (d, *J* = 10.1 Hz, 2H, pyran-CH), 4.47 (m, 4H, CH_2-5), 3.80 (m, 4H, CH_2-4), 3.52 (t, *J* = 6.7 Hz, CH_2-3), 2.49 (s, 6H, $ArCH_3$), 1.67 (m, 4H, CH_2-2), 0.64 (m, 4H, CH_2-1), 0.14-0.08 (m, $SiCH_3$) ppm.



Telechelic poly(dimethylsiloxane) conjugated 2-Phenyl-2-(4-piperidinophenyl)-5-(2-hydroxyethoxycarbonyl)-9-dimethylamino-2*H*-naphtho[1,2-*b*]pyran, 25. This conjugate was synthesized using *Method A*. The conjugate was obtained after purification using a chromatotron (silica gel, 2%MeOH/CH_2Cl_2→4%MeOH/CH_2Cl_2) and fractionated using a chromatotron (silica gel, 1.5%MeOH/CH_2Cl_2). Average molecular weights were determined by ^{1}H NMR analysis. Nonfractionated product, **25**: M_n = 2,571 (n_{PDMS} = 14.1). Fraction 1, **25a**: M_n = 3,179 (n_{PDMS} = 22.3). Fraction 2, **25b**: M_n = 2,405 (n_{PDMS} = 11.9). Fraction 3, **25c**: M_n = 2,213 (n_{PDMS} = 9.3). ^{1}H NMR (200 MHz, *d*$_6$-acetone) δ 8.03 (s, 2H), 7.77 (d, *J* = 9.1 Hz, 2H), 7.71 (d, *J* = 10.1 Hz, 2H, pyran-CH), 7.59 (m, 4H), 7.41-7.19 (m, 14H), 6.85 (d, *J* = 8.9 Hz, 4H), 6.37 (d, *J* = 10 Hz, 2H), 4.49 (m, 8H, CH_2-8,9), 4.13 (t, *J* = 4.9 Hz, 4H, CH_2-5), 3.53 (t, *J* = 4.9 Hz, 4H, CH_2-4), 3.37 (t, *J* = 6.8 Hz, 4H, CH_2-3), 3.11 (m, 20H, NCH_2 and NCH_3), 2.66 (s, 8H, CH_2-6,7), 1.56 (m, 16H, piperidine-CH_2 and CH_2-2), 0.57 (m, 4H, CH_2-1), 0.12-0.08 (m, $SiCH_3$) ppm.

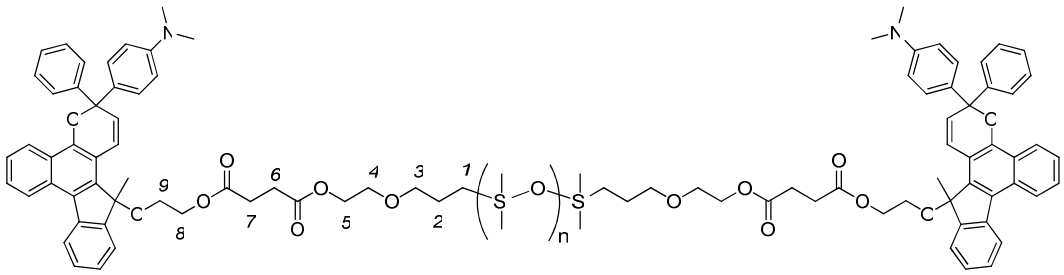


Telechelic poly(dimethylsiloxane) conjugated 2,2-Bis(4-dimethylaminophenyl)-5-(2-hydroxyethoxycarbonyl)-9-dimethylamino-2*H*-naphtho[1,2-*b*]pyran, 28. This conjugate was synthesized using *Method B* and purified by column chromatography (silica gel, 10%diethyl ether/CH_2Cl_2→30%diethyl ether/CH_2Cl_2). Fractionation was performed by column chromatography (silica gel, diethyl ether). Average molecular weights were determined by ^{1}H NMR analysis. Nonfractionated product, **28**: M_n = 2,550 (n_{PDMS} = 13.7). Fraction 1, **28a**: M_n = 2,623 (n_{PDMS} = 23.9). Fraction 2, **28b**: M_n = 2,196 (n_{PDMS} = 18.1). Fraction 3, **28c**: M_n = 1,853 (n_{PDMS} = 13.5). Fraction 4, **28d**: M_n = 1,550 (n_{PDMS} = 9.4). ^{1}H NMR (400 MHz, d_6-acetone) δ 8.01 (s, 2H), 7.75 (d, *J* = 9.1 Hz, 2H), 7.65 (d, *J* = 10.0 Hz, 2H), 7.35 (m, *J* = 8.8 Hz, 10H), 7.23 (broad d, *J* = 9.0 Hz, 2H), 6.66 (d, *J* = 8.8 Hz, 8H), 6.29 (d, *J* = 10.0 Hz, 2H), 4.50 (m, 4H, CH_2-8), 4.46 (m, 4H, CH_2-9), 4.13 (t, *J* = 5.0 Hz, 4H, CH_2-5), 3.54 (t, *J* = 5.0 Hz, 4H, CH_2-4) 3.37 (t, *J* = 6.7 Hz, 4H, CH_2-3), 3.12 (s, 12H, naphthyl-NCH_3), 2.88 (s, 24H, geminal-$PhN(CH_3)_2$), 2.66 (m, 8H, CH_2-6,7), 1.58 (m, 4H, CH_2-2), 0.57 (m, 4H, CH_2-1), 0.13-0.08 (m, $SiCH_3$) ppm.



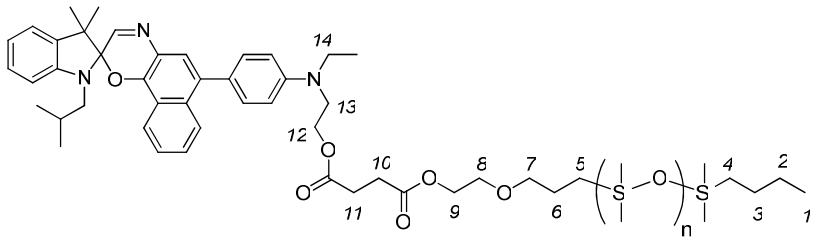
Telechelic poly(dimethylsiloxane) conjugated 2,2-Diphenyl-5-methoxycarbonyl-6-hydroxy-3,4-dihydro-2*H*-naphtho[1,2-b]pyran, 33. This

conjugate was synthesized using *Method B* and purified by column chromatography (silica gel, EtOAc/hexane, 1:6 initially to remove unreacted starting dihydropyran, then 1:1). Fractionation was performed by column chromatography (silica gel, diethyl ether/hexane, 2:1). Only one, front-running fraction collected. Average molecular weights were determined by ^{1}H NMR analysis. Fraction 1, **33**: M_n = 2,904 (n_{PDMS} = 22.3). ^{1}H NMR (400 MHz, d_6-acetone) δ 8.60 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.73 (m, 2H), 7.66-7.61 (m, 10H), 7.34 (m, 8H), 7.24 (m, 4H), 4.24 (m, 4H, CH_2-5), 3.86 (s, 6H, OCH_3), 3.63 (m, 4H, CH_2-4), 3.42 (t, *J* = 6.8 Hz, 4H, CH_2-3), 3.02 (m, 4H, dihydropyran-CH_2), 2.87 (m, 8H, CH_2-6,7), 2.78 (m, 4H, dihydropyran-CH_2), 1.61 (m, 4H, CH_2-2), 0.58 (m, 4H, CH_2-1), 0.13-0.09 (m, $SiCH_3$) ppm.

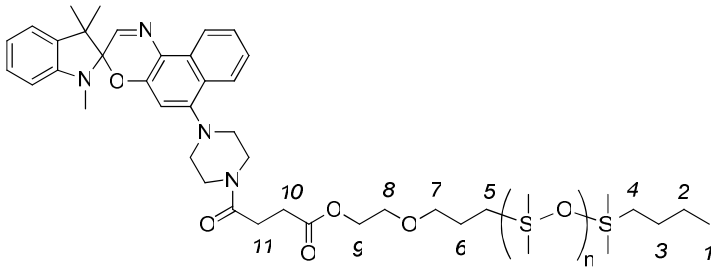


Telechelic poly(dimethylsiloxane) conjugated 3-(4-Dimethylaminophenyl)-3-phenyl-13-methyl-13-(2-hydroxyethoxy)-indeno[2,1-*f*]naphtho[1,2-*b*]pyran, 35a and 35b. This conjugate was synthesized via *Method A*, using a pre-fractionated carboxylic acid-terminated poly(dimethylsiloxane) having a high average molecular weight (M_n = 2,503). Two product fractions were collected upon purification by column chromatography (silica gel, EtOAc/petroleum ether, 1:2). Average molecular weights were determined by ^{1}H NMR analysis: Fraction 1, **35a**: M_n = 3,999 (n_{PDMS} = 33.6), Fraction 2, **35b**: M_n = 3,221 (n_{PDMS} = 23.1). ^{1}H NMR (400 MHz, d_6-acetone) δ 8.66 (d, *J* = 8.4 Hz, 2H), 8.50 (d, *J* = 8.4 Hz, 2H), 8.21 (d, *J* = 7.8 Hz, 2H), 7.66-7.54 (m, 12H), 7.45-7.21 (m, 14H), 6.68 (d, *J* = 8.9 Hz, 2H), 6.62 (d, *J* = 8.9 Hz, 2H), 6.44-6.37 (2 × d, *J* = 9.9 Hz, 2H, pyran-CH), 4.17-4.07 (m, 8H, CH_2-5,8), 3.57 (m, 4H, CH_2-4), 3.40 (t, *J* = 6.8 Hz, 4H, CH_2-3), 3.06 (m, 4H, CH_2-9), 2.89 (s, 6H, NCH_3), 2.84 (s, 6H, NCH_3), 2.68-2.52 (m, 8H, CH_2-6,7), 1.75 and 1.73 (2 × s, 6H, indeno-CH_3), 1.60 (m, 4H, CH_2-2), 0.58 (m, 4H, CH_2-1), 0.14-0.09 (m, $SiCH_3$) ppm.

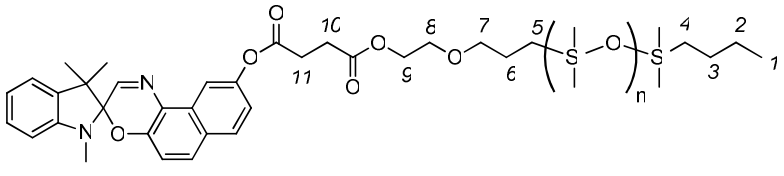
Mono End-Functional Photochromic Dye-Poly(Dimethylsiloxane) Conjugates



Mono end-functional poly(dimethylsiloxane) conjugated 1,3-Dihydro-1-isobutyl-3,3-dimethyl-6'-(4-(*N*-ethyl, *N*-(2-hydroxyethyl)amino)phenyl)-spiro[2*H*-indole-2,2'[2*H*]naphtha[1,2-*b*][1,4]oxazine, 2. This conjugate was synthesized using *Method A* for telechelic conjugates, adjusting the stoichiometry of reagents accordingly for use of mono carboxylic acid end-terminated PDMS.[6] The pure conjugate was obtained after column chromatography (silica gel, 0-20% EtOAc/petroleum ether) as a green oil. A sample of the material was fractionated by column chromatography using the same solvent system. Average molecular weights were determined by ^{1}H NMR analysis. Nonfractionated product, **2**: M_n = 1,677 (n_{PDMS} = 11.4). Fraction 1, **2a**: M_n = 1,952 (n_{PDMS} = 15.1). Fraction 2, **2b**: M_n = 1,588 (n_{PDMS} = 10.2). Fraction 3, **2c**: M_n = 1,365 (n_{PDMS} = 7.2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-7.91 (m, 2H), 7.72 (s, 1H), 7.45 (s, 1H), 7.41-7.33 (m, 4H), 7.21 (dt, *J* = 7.7, 1.2 Hz, 1H), 7.09 (dd, *J* = 7.3, 0.9 Hz, 2H), 6.90 (dt, *J* = 7.7, 1.2 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.61 (d, *J* = 7.8 Hz, 1H), 4.33 (t, *J* = 6.5 Hz, 2H, CH_2-12), 4.25 (t, *J* = 5.0 Hz, 4H, CH_2-9), 3.65-3.59 (m, 4H, CH_2-8,13), 3.51-3.40 (m, 4H, CH_2-7,14), 2.98 (ddd, *J* = 23.5, 14.5, 7.6 Hz, 2H, isobutyl-CH_2), 2.71-2.64 (m, 4H, CH_2-10,11), 2.12-2.06 (m, 1H, isobutyl-CH), 1.68-1.57 (m, 2H, CH_2-6), 1.39 (2 × s, 6H, spirooxazine geminal-CH_3), 1.35-1.21 (m, 7H, ethyl-CH_3 and CH_2-2,3), 0.98 (d, *J* = 6.6 Hz, 3H, isobutyl-CH_3), 0.90-0.86 (m, 6H, isobutyl-CH_3 and CH_3-1), 0.55-0.49 (m, 4H, CH_2-4,5), 0.10-0.04 (m, $SiCH_3$) ppm. Refer to graphic above for corresponding numbering system used in NMR assignments.

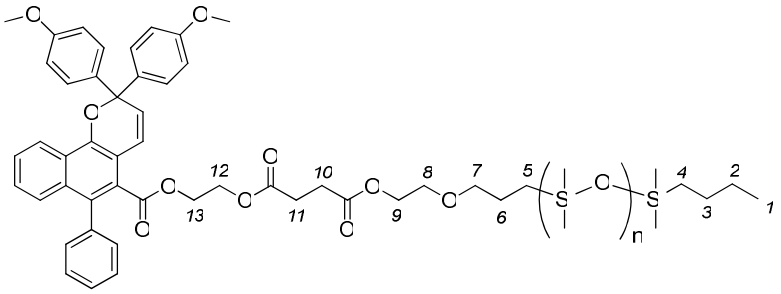


Mono end-functional poly(dimethylsiloxane) conjugated 6'-Piperazine-1,3,3-trimethylspiro[indoline-2,3'-[3*H*] naphtho[2,1-*b*][1,4]oxazine, 5. This conjugate was synthesized by reaction of 6'-Piperazine-1,3,3-trimethylspiro[indoline-2,3'-[3*H*] naphtho[2,1-*b*][1,4]oxazine with mono acid chloride end-terminated PDMS using the literature procedure.[6] The pure conjugate was obtained after column chromatography (silica gel, diethyl ether/hexane, 1:1→2:1). A sample of the material was fractionated by column chromatography (silica gel, diethyl ether/hexane, 2:1). Average molecular weights were determined by ^{1}H NMR analysis. Nonfractionated product, **5**: M_n = 1,634 (n_{PDMS} = 12.2). Fraction 1, **5a**: M_n = 1,849 (n_{PDMS} = 15.3). Fraction 2, **5b**: M_n = 1,383 (n_{PDMS} = 9.0). Fraction 3, **5c**: M_n = 1,151 (n_{PDMS} = 5.9). ^{1}H NMR (400 MHz, d_6-acetone) δ 8.59 (d, 1H), 8.14 (d, 1H), 7.70 (s, 1H), 7.57 (m, 1H), 7.41 (m, 1H), 7.17 (td, 1H), 7.12 (d, 1H), 6.85 (t, 1H), 6.66 (s, 1H), 6.62 (d, 1H), 4.16 (m, 2H, CH_2-9), 3.79 (s br, piperazine-CH), 3.60 (m, 2H, CH_2-8), 3.42 (t, 2H, CH_2-7), 3.10 (s br, piperazine-CH), 3.03 (s br, piperazine-CH), 2.73 (s, 3H, NCH_3), 2.68 (m, 2H, CH_2-11), 2.60 (m, 2H, CH_2-10), 1.61 (m, 2H, CH_2-6), 1.37-1.32 (m, 10H, spirooxazine geminal CH_3 and CH_2-2,3), 0.89 (t, 3H, CH_3-1), 0.59 (m, 4H,CH_2-4,5), 0.12-0.08 (m, $SiCH_3$) ppm.



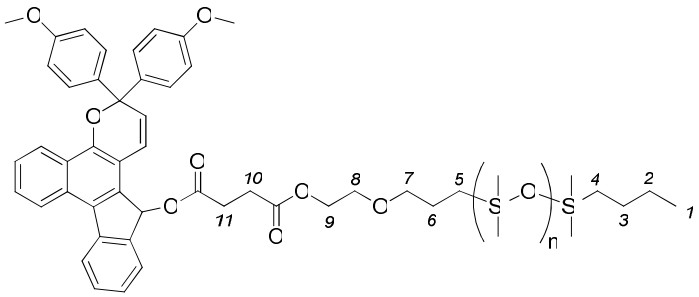
Mono end-functional poly(dimethylsiloxane) conjugated 9'-Hydroxy-1,3,3-trimethylspiro[indoline-2,3'-[3*H*]-naphtho[2,1-*b*][1,4]oxazine], 8. This conjugate was synthesized by reaction of 9'-Hydroxy-1,3,3-trimethylspiro[indoline-2,3'-[3*H*]-

naphtho[2,1-*b*][1,4]oxazine] with mono acid chloride end-terminated PDMS using the literature procedure.[6] The pure conjugate was obtained after column chromatography (silica gel, diethyl ether/hexane, 1:3) as a viscous green oil. Fractionation was performed by column chromatography using the same solvent system. Average molecular weights were determined by ^{1}H NMR analysis. Nonfractionated product, **8**: M_n = 1,550 (n_{PDMS} = 12.2). Fraction 1, **8a**: M_n = 1,784 (n_{PDMS} = 15.4). Fraction 2, **8b**: M_n = 1,381 (n_{PDMS} = 9.9). Fraction 3, **8c**: M_n = 1,106 (n_{PDMS} = 6.2). ^{1}H NMR (200 MHz, d_6-acetone) δ 8.25 (d, *J* = 2.56 Hz, 1H), 7.88 (d, *J* = 8.77 Hz, 1H), 7.83 (s overlapping, 1H), 7.81 (d overlapping, 1H), 7.18 (m, 3H), 7.04 (d, *J* = 8.77 Hz, 1H), 6.86 (t, *J* = 7.68 Hz, 1H), 6.66 (d, *J* = 7.68 Hz, 1H), 4.25 (t, *J* = 5.12 Hz, 2H, CH_2-9), 3.65 (t, *J* = 5.12 Hz, 2H, CH_2-8), 3.44 (t, *J* = 6.94 Hz, 2H, CH_2-7), 2.99 (t, *J* = 6.94 Hz, 2H, CH_2-11), 2.80 (t overlapping, 2H, CH_2-10), 2.77 (s overlapping, 3H, CH_3N), 1.62 (m, 2H, CH_2-6), 1.35 (m overlapping, 10H, spirooxazine geminal-CH_3 and CH_2-2,3), 0.89 (t, *J* = 7.31 Hz, 3H, CH_3-1), 0.59 (m, 4H, CH_2-4,5), 0.10 (m, $SiCH_3$) ppm.

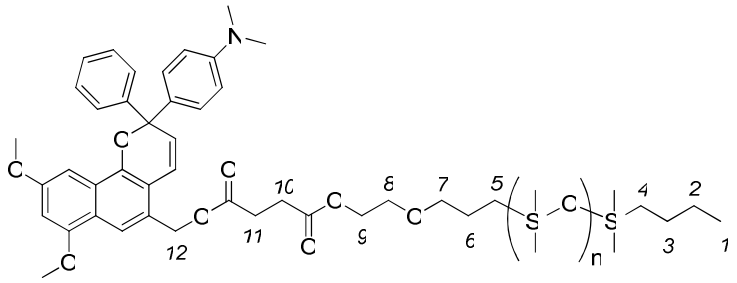


Mono end-functional poly(dimethylsiloxane) conjugated 2,2-Bis(4-methoxyphenyl)-5-(2-hydroxyethoxycarbonyl)-6-phenyl-2*H*-naptho[1,2-*b*]pyran, 11. This conjugate was synthesized by reaction of 2,2-Bis(4-methoxyphenyl)-5-(2-hydroxyethoxycarbonyl)-6-phenyl-2*H*-naptho[1,2-*b*]pyran with mono acid chloride end-terminated PDMS using the literature procedure.[6] The pure conjugate, a viscous pink oil, was obtained after column chromatography (silica gel, diethyl ether/hexane, 1:1). Fractionation was performed by column chromatography using the same solvent system. Average molecular weights were determined by ^{1}H NMR analysis. Nonfractionated product, **11**: M_n = 1,830 (n_{PDMS} = 13.1). Fraction 1, **11a**: M_n = 2,461 (n_{PDMS} = 21.6). Fraction 2, **11b**: M_n = 1,949 (n_{PDMS} = 14.7). Fraction 3, **11c**: M_n = 1,507 (n_{PDMS} = 8.7). ^{1}H NMR (400 MHz, d_6-acetone) δ 8.46 (d, *J* = 8.4 Hz, 1H), 7.61

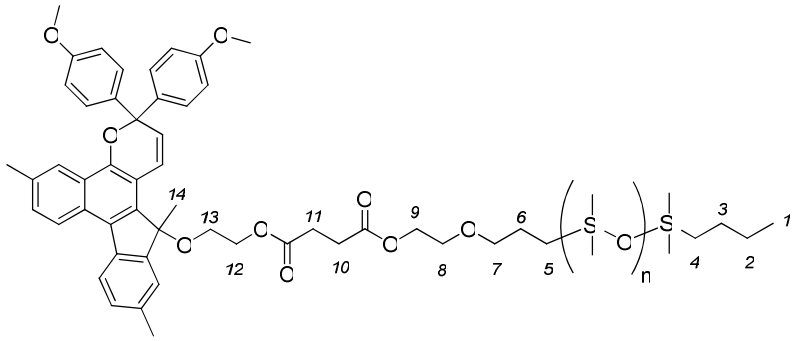
(m, 1H), 7.44-7.50 (m, 9H), 7.32 (m, 2H), 6.92 (d, *J* = 8.9 Hz, 4H), 6.85 (d, *J* = 10 Hz, 1H, pyran-CH), 6.45 (d, *J* = 10 Hz, 1H, pyran-CH), 4.19 (m, 2H, CH_2-12), 4.14 (t, *J* = 5.0 Hz, 2H, CH_2-9), 3.99 (m, 2H, CH_2-13), 3.77 (s, 6H, CH_3OAr), 3.54 (t, *J* = 5.0 Hz, 2H, CH_2-8), 3.38 (t, *J* = 6.8 Hz, 2H, CH_2-7), 2.62 (s, 4H, CH_2-10,11), 1.59 (m, 2H, CH_2-6), 1.37 (m, 4H, CH_2-2,3), 0.90 (t, *J* = 6.9 Hz, 3H, CH_3-1), 0.59 (m, 4H, CH_2-4,5), 0.09-0.13 (m, $SiCH_3$) ppm.



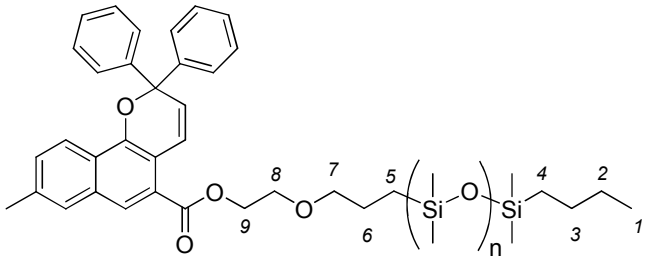
Mono end-functional poly(dimethylsiloxane) conjugated 3,3-Bis(4-methoxyphenyl)-13-hydroxy-indeno[2,1-*f*]naphtho[1,2-*b*]pyran, 14. This conjugate was synthesized by reaction of 3,3-Bis(4-methoxyphenyl)-13-hydroxy-indeno[2,1-*f*]naphtho[1,2-*b*]pyran with mono acid chloride end-terminated PDMS using the literature procedure.[6] The pure conjugate, a viscous dark-purple oil, was obtained after column chromatography (silica gel, chloroform/hexane, 5:4→neat $CHCl_3$). Fractionation was performed by column chromatography (silica gel, Et_2O/hexane, 1:1). Average molecular weights were determined by ^{1}H NMR analysis. Nonfractionated product, **14**: M_n = 1,716 (n_{PDMS} = 12.4). Fraction 1, **14a**: M_n = 2,256 (n_{PDMS} = 19.7). Fraction 2, **14b**: M_n = 1,981 (n_{PDMS} = 15.9). Fraction 3, **14c**: M_n = 1,680 (n_{PDMS} = 11.9). Fraction 4, **14d**: M_n = 1,438 (n_{PDMS} = 8.6). Fraction 5, **14e**: M_n = 1,260 (n_{PDMS} = 6.2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.4 Hz, 1H), 8.43 (d, 8.4 Hz, 1H), 8.09 (d, *J* = 7.8 Hz, 1H), 7.50-7.60 (m, 3H), 7.39-7.44 (m, 5H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.04 (s, 1H, indeno-CH), 6.81-6.85 (m, 5H), 6.23 (d, *J* = 9.9 Hz, 1H, pyran-CH), 4.25 (t, *J* = 4.9 Hz, 2H, CH_2-9), 3.76 and 3.77 (2 × s overlapping, 6H, CH_3OAr), 3.59 (t, *J* = 4.9 Hz, 2H, CH_2-8), 3.39 (t, *J* = 7.1 Hz, 2H, CH_2-7), 2.69-2.83 (m, 4H, CH_2-10,11), 1.60 (m, 2H, CH_2-6), 1.32 (m, 4H, CH_2-2,3), 0.88 (t, *J* = 6.9 Hz, 3H, CH_3-1), 0.52 (m, 4H, CH_2-4,5), 0.04-0.08 (m, approx. 82H, $SiCH_3$) ppm.



Mono end-functional poly(dimethylsiloxane) conjugated 2-(4-Dimethylaminophenyl)-2-phenyl-5-hydroxymethyl-7,9-dimethoxy-2*H*-naphtho[1,2-*b*]pyran, 17. This conjugate was synthesized by reaction of 2-(4-Dimethylaminophenyl)-2-phenyl-5-hydroxymethyl-7,9-dimethoxy-2*H*-naphtho[1,2-*b*]pyran with mono acid chloride end-terminated PDMS using the literature procedure.[6] Purification by column chromatography (silica gel, diethyl ether/hexane, 1:3) gave the pure product as a deep blue oil. Fractionation was performaed by column chromatography (silica gel, diethyl ether/hexane, 4:1). Average molecular weights were determined by ^{1}H NMR analysis. Nonfractionated product, **17**: M_n = 1,672 (n_{PDMS} = 12.2). Fraction 1, **17a**: M_n = 2,012 (n_{PDMS} = 16.8). Fraction 2, **17b**: M_n = 1,699 (n_{PDMS} = 12.6). Fraction 3, **17c**: M_n = 1,430 (n_{PDMS} = 8.9). ^{1}H NMR (200 MHz, d_6-acetone) δ 7.66 (s, 1H), 7.57 (m, 2H), 7.24-7.34 (m, 6H), 6.99 (d, *J* = 9.9 Hz, 1H), 6.68 (m, 2H), 6.58 (d, *J* = 2.2 Hz, 1H), 6.39 (d, *J* = 9.9 Hz, 1H), 5.27 (s, 2H, CH_2-12), 4.16 (t, *J* = 4.0 Hz, 2H, CH_2-9), 3.96 (s, 3H, OCH_3), 3.93 (s, 3H, OCH_3), 3.56 (t, *J* = 4.0 Hz, 2H, CH_2-8), 3.38 (t, *J* = 7.0 Hz, 2H, CH_2-7), 2.87 (s, 6H, $N(CH_3)_2$), 2.63 (s, 4H, CH_2-10,11), 1.60 (m, 2H, CH_2-6), 1.36 (m, CH_2-2,3), 0.89 (t, *J* = 7.3 Hz, 3H, CH_3-1), 0.58 (m, 4H, CH_2-4,5), 0.09 (m, $SiCH_3$) ppm.

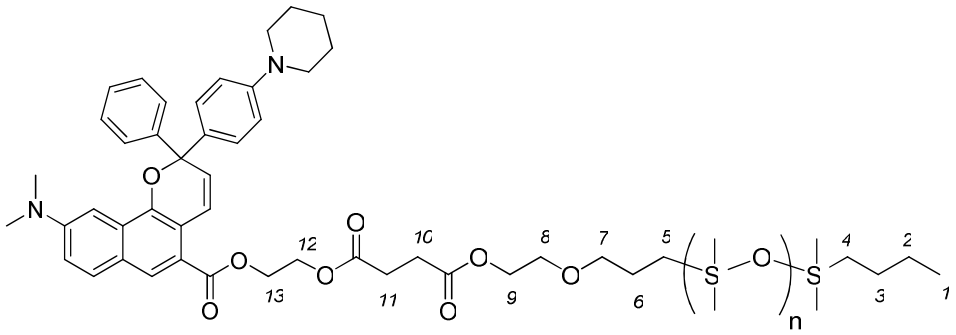


Mono end-functional poly(dimethylsiloxane) conjugated 3,3-Bis(4-methoxyphenyl)-6,11,13-trimethyl-13-(2-hydroxyethoxy)-indeno[2,1-*f*] naphtho[1,2-*b*]pyran, 20. This conjugate was synthesized using *Method A* for telechelic conjugates, adjusting the stoichiometry of reagents accordingly for use of mono carboxylic acid end-terminated PDMS.[6] The pure conjugate was obtained after purification using a chromatotron (silica gel, 100%CH_2Cl_2→1%MeOH/CH_2Cl_2) and fractionated using a chromatotron (silica gel, 10% ethyl acetate/petroleum ether). Average molecular weights were determined by ^{1}H NMR analysis. Nonfractionated product, **20**: M_n = 1,849 (n_{PDMS} = 13.0). Fraction 1, **20a**: M_n = 2,224 (n_{PDMS} = 18.1). Fraction 2, **20b**: M_n = 1,893 (n_{PDMS} = 13.6). Fraction 3, **20c**: M_n = 1,650 (n_{PDMS} = 10.3). Fraction 4, **20d**: M_n = 1,416 (n_{PDMS} = 7.2). ^{1}H NMR (400 MHz, d_6-acetone) δ 8.52 (d, *J* = 8.6 Hz, 1H), 8.25 (s, 1H), 8.06 (d, *J* = 7.9 Hz, 1H), 7.53-7.45 (m, 6H), 7.37 (s, 1H), 7.25 (d, *J* = 7.8 Hz, 1H), 6.92 (m, *J* = 8.9 Hz, 2H), 6.86 (m, *J* = 8.9 Hz, 2H), 6.42 (d, *J* = 9.9 Hz, 1H, pyran-CH), 4.14 (t, *J* = 5.0 Hz, 2H, CH_2-9), 4.08 (t, *J* = 4.9 Hz, 2H, CH_2-12), 3.78 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3), 3.57 (t, *J* = 5.0 Hz, 2H, CH_2-8), 3.39 (t, *J* = 6.8 Hz, 2H, CH_2-7), 3.04 (m, 2H, CH_2-13), 2.60 (m, 4H, CH_2-10,11), 2.55 (s, 3H, $ArCH_3$), 2.42 (s, 3H, $ArCH_3$), 1.70 (s, 3H, CH_3-14), 1.59 (m, 2H, CH_2-6), 1.35 (m, 4H, CH_2-2,3), 0.87 (m, 3H, CH_3-1), 0.58 (m, 4H, CH_2-4,5), 0.12-0.08 (m, $SiCH_3$) ppm.



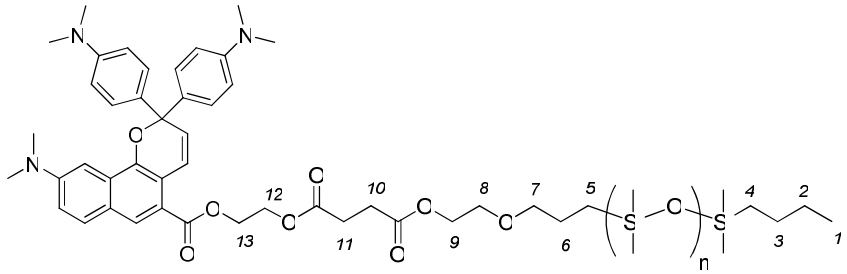
Mono end-functional poly(dimethylsiloxane) conjugated 2,2-Diphenyl-5-carboxylic acid-8-methyl-2*H*-naphtho[1,2-*b*]pyran, 23. This conjugate was synthesized using *Method A* for telechelic conjugates, adjusting the stoichiometry of reagents accordingly for use of mono hydroxyl end-terminated PDMS. The pure product was obtained after column chromatography (silica gel, EtOAc/petroleum ether, 1:4). Fractionation was performed by column chromatography (silica gel,

5→10%EtOAc/petroleum ether). Average molecular weights were determined by ^{1}H NMR analysis. Nonfractionated product, **23**: M_n = 1,568 (n_{PDMS} = 13.2). Fraction 1, **23a**: M_n = 1,965 (n_{PDMS} = 18.5). Fraction 2, **23b**: M_n = 1,479 (n_{PDMS} = 12.0). Fraction 3, **23c**: M_n = 1,185 (n_{PDMS} = 8.0). Fraction 4, **23d**: M_n = 1,085 (n_{PDMS} = 6.6). ^{1}H NMR (400 MHz, *d*$_6$-acetone) δ 8.37 (d, *J* = Hz, 1H), 8.03 (s, 1H), 7.70 (d overlap, 1H), 7.69 (s overlap, 1H), 7.60-7.58 (m, 4H), 7.54 (dd, *J* = Hz, 1H), 7.36-7.31 (m, 4H), 7.25 (m, 2H), 6.45 (s, 1H, pyran-CH), 4.47 (m, 2H, CH_2-9), 3.80 (m, 2H, CH_2-8), 3.52 (t, *J* = Hz, 2H, CH_2-7), 2.51 (s, 3H, $ArCH_3$), 1.67 (m, 2H, CH_2-6), 1.36 (m, 4H, CH_2-2,3), 0.89 (m, 3H, CH_3-1), 0.66-0.57 (m, 4H, CH_2-4,5), 0.13-0.07 (m, $SiCH_3$) ppm.

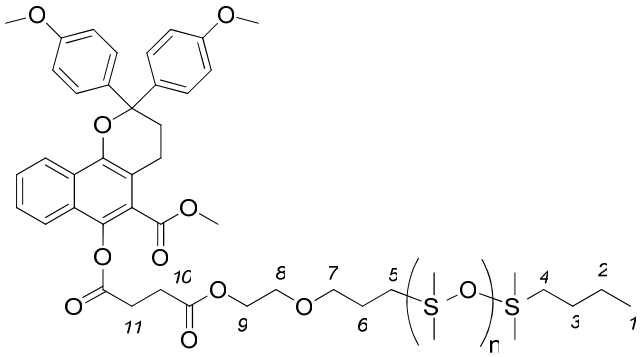


Mono end-functional poly(dimethylsiloxane) conjugated 2-Phenyl-2-(4-piperidinophenyl)-5-(2-hydroxyethoxycarbonyl)-9-dimethylamino-2*H*-naphtho[1,2-*b*]pyran, 26. This conjugate was synthesized using *Method A* for telechelic conjugates, adjusting the stoichiometry of reagents accordingly for use of mono carboxylic acid end-terminated PDMS.[6] The pure conjugate was obtained after purification using a chromatotron (silica gel, 2%MeOH/CH_2Cl_2→4%MeOH/CH_2Cl_2) and fractionated using a chromatotron (silica gel, 1%MeOH/CH_2Cl_2). Average molecular weights were determined by ^{1}H NMR analysis. Nonfractionated product, **26**: M_n = 1,843 (n_{PDMS} = 13.4). Fraction 1, **26a**: M_n = 2,099 (n_{PDMS} = 16.9). Fraction 2, **26b**: M_n = 1,838 (n_{PDMS} = 13.3). Fraction 3, **26c**: M_n = 1,574 (n_{PDMS} = 9.8). ^{1}H NMR (200 MHz, *d*$_6$-acetone) δ 8.03 (s, 1H), 7.78 (d, *J* = 9.1 Hz, 1H), 7.71 (d, *J* = 10.1 Hz, 1H, pyran-CH), 7.59 (m, 2H), 7.42-7.23 (m, 7H), 6.86 (m, *J* = 9 Hz, 2H), 6.38 (d, *J* = 10 Hz, 1H), 4.49 (m, 4H, CH_2-12,13), 4.13 (t, *J* = 5 Hz, 2H, CH_2-9), 3.54 (t, *J* = 5 Hz, 2H, CH_2-8), 3.37 (t, *J* = 6.8 Hz, 2H, CH_2-7), 3.15-3.09 (m, 10H, NCH_3 and NCH_2), 2.67 (m, 4H, CH_2-10,11), 1.57 (m, 8H, piperidine-CH_2 and CH_2-6), 1.37

(m, 4H, CH_2-2,3), 0.89 (t, *J* = 7 Hz, 3H, CH_3-1), 0.58 (m, 4H, CH_2-4,5), 0.14-0.08 (m, $SiCH_3$) ppm.

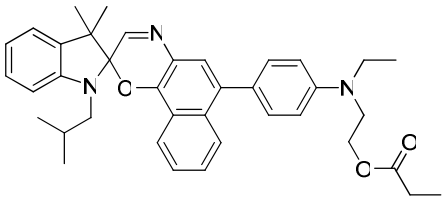


Mono end-functional poly(dimethylsiloxane) conjugated 2,2-Bis(4-dimethylaminophenyl)-5-(2-hydroxyethoxycarbonyl)-9-dimethylamino-2*H*-naphtho[1,2-*b*]pyran, 29. This conjugate was synthesized by reaction of 2,2-Bis(4-dimethylaminophenyl)-5-(2-hydroxyethoxycarbonyl)-9-dimethylamino-2*H*-naphtho[1,2-*b*]pyran with mono acid chloride end-terminated PDMS using the literature procedure.[6] The pure conjugate was obtained after purification by column chromatography (silica gel, diethyl ether/CH_2Cl_2, 1:9). Fractionation was performed by column chromatography (silica gel, diethyl ether/hexane, 3:1). Average molecular weights were determined by ^{1}H NMR analysis. Nonfractionated product, **29**: M_n = 1,791 (n_{PDMS} = 12.7). Fraction 1, **29a**: M_n = 2,240 (n_{PDMS} = 18.7). Fraction 2, **29b**: M_n = 1,904 (n_{PDMS} = 14.2). Fraction 3, **29c**: M_n = 1,555 (n_{PDMS} = 9.5). Fraction 4, **29d**: M_n = 1,312 (n_{PDMS} = 6.2). ^{1}H NMR (400 MHz, d_6-acetone) δ 8.01 (s, 1H), 7.74 (d, *J* = 9.1 Hz, 1H), 7.66 (d, *J* = 10.1 Hz, 1H, pyran-CH), 7.36 (m, 5H), 7.22 (dd, *J* = 9.1, 2.7 Hz, 1H), 6.66 (m, *J* = 8.9 Hz, 4H), 6.29 (d, *J* = 10.1 Hz, 1H, pyran-CH), 4.51 (m, 2H, CH_2-12), 4.46 (m, 2H, CH_2-13), 4.14 (t, *J* = 5 Hz, 2H, CH_2-9), 3.54 (t, *J* = 5 Hz, 2H, CH_2-8), 3.38 (t, *J* = 6.8 Hz, 2H, CH_2-7), 3.11 (s, 6H, naphthyl-$N(CH_3)_2$), 2.87 (s, 12H, *geminal*-$PhN(CH_3)_2$), 2.67 (m, 4H, CH_2-10,11), 1.59 (m, 2H, CH_2-6), 1.37 (m, 4H, CH_2-2,3), 0.91 (t, *J* = 7 Hz, 3H, CH_3-1), 0.59 (m, 4H, CH_2-4,5), 0.14-0.10 (m, $SiCH_3$) ppm.

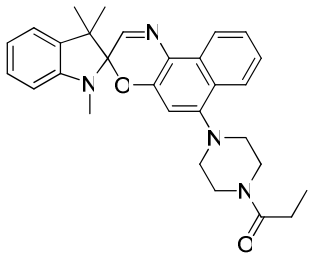


Mono end-functional poly(dimethylsiloxane) conjugated 2,2-Bis(4-methoxyphenyl)-5-methoxycarbonyl-6-hydroxy-3,4-dihydro-2*H*-naphtho[1,2-b]pyran, 34. This conjugate was synthesized by reaction of 2,2-Bis(4-methoxyphenyl)-5-methoxycarbonyl-6-hydroxy-3,4-dihydro-2*H*-naphtho[1,2-b]pyran with mono acid chloride end-terminated PDMS using the literature procedure.[6] The crude residue was dissolved in acetone and passed through basic alumina to remove unreacted starting dihydro-naphthopyran. The pure conjugate was obtained after purification by column chromatography (silica gel, EtOAc/hexane, 1:2). Average molecular weight was determined by ^{1}H NMR analysis. Nonfractionated product, **34**: M_n = 1,675 (n_{PDMS} = 12.2). ^{1}H NMR (400 MHz, d_6-acetone) δ 8.53 (d, J = 8.4 Hz, 1H), 7.95 (d, J = 8.1 Hz, 1H), 7.70 (m, 1H), 7.61 (m, 1H), 7.49 (m, 4H), 6.88 (m, 4H), 4.24 (m, 2H, CH_2-9), 3.87 (s, 3H, $COOCH_3$), 3.75 (s, 6H, $ArOCH_3$), 3.63 (m, 2H, CH_2-8), 3.42 (t, J = 6.8 Hz, 2H, CH_2-7), 3.02 (m, 2H, dihydropyran-CH_2), 2.81 (m, 4H, CH_2-10,11), 2.77 (m, 2H, dihydropyran-CH_2), 1.61 (m, 2H, CH_2-6), 1.36 (m, 4H, CH_2-2,3), 0.90 (t, 3H, butyl-CH_3), 0.59 (m, 4H, CH_2-4,5), 0.13-0.09 (m, $SiCH_3$) ppm.

Photochromic Control Compounds

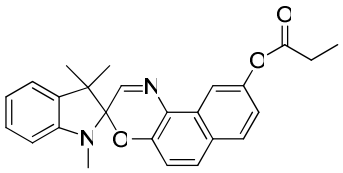


2-(*N*-Ethyl-*N*-(4-(1-isobutyl-3,3-dimethylspiro[indoline-2,2'-naphtho[1,2-b][1,4]oxazine]-6'-yl)phenyl)amino)ethyl propionate, 3. This compound was synthesized from 1,3-Dihydro-1-isobutyl-3,3-dimethyl-6'-(4-(*N*-ethyl, *N*-(2-hydroxyethyl)amino)phenyl)-spiro[2*H*-indole-2,2'[2*H*]naphtha[1,2-*b*][1,4]oxazine] using the literature procedure.[6] Purified by column chromatography (silica gel, 0-10% v/v EtOAc/petroleum ether).Yield: >95%. MPt: 60-64 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.08-7.89 (m, 2H), 7.73 (s, 1H), 7.46 (s, 1H), 7.42-7.07 (m, 6H), 6.93-6.80 (m, 3H), 6.61 (d, *J* = 7.8 Hz, 1H), 4.31 (t, *J* = 6.4 Hz, 2H), 3.64 (t, *J* = 6.4 Hz, 2H) 3.49 (q, *J* = 7.0 Hz, 2H), 3.06-2.83 (m, 2H), 2.38 (q, *J* = 7.6 Hz, 2H), 1.39 (d, *J* = 3.7 Hz, 6H), 1.29-1.12 (m, 6H), 0.99-0.89 (m, 6H) ppm. MS (EI): *m/z* = 589.3 [M^+]; (HR, EI): *m/z* 589.3289 ($C_{38}H_{43}N_3O_3$ [M^+] requires: 589.3299).

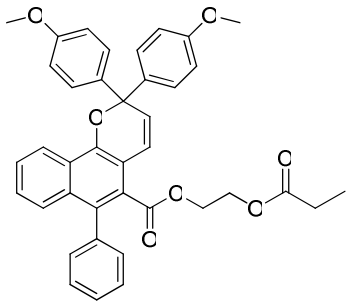


6'-(4-Propionylpiperazin-1-yl)-1,3,3-trimethylspiro[indoline-2,3'-[3*H*]-naphtho[2,1-*b*][1,4]-oxazine, 6. This compound was synthesized from 6'-Piperazine-1,3,3-trimethylspiro[indoline-2,3'-[3*H*] naphtho[2,1-*b*][1,4]oxazine using the literature procedure.[6] Purified by column chromatography (silica gel, diethyl ether). Yield: 92%. ^{1}H NMR (400 MHz, d_6-acetone) δ 8.58 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8.4 Hz, 1H), 7.71 (s, 1H), 7.57 (m, 1H), 7.41 (m, 1H), 7.17 (m, 1H), 7.13 (d, *J* = 7.3 Hz, 1H), 6.85 (m, 1H), 6.66 (s, 1H), 6.63 (d, *J* = 7.7 Hz, 1H), 3.77 (br s, piperazyl-CH), 3.06 (br d, piperazyl-CH), 2.81 (br s, piperazyl-CH), 2.74 (s, 3H, NCH_3), 2.39

(q, J = 7.3 Hz, 2H, propionyl-CH_2), 1.33 (2 × s overlap, 6H, *gem*-CH_3), 1.06 (t, J = 7.3 Hz, 3H, propionyl-CH_3) ppm.

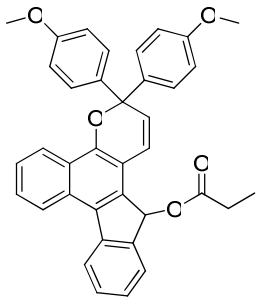


9'-Propionyloxy-1,3,3-trimethylspiro[indoline-2,3'-[3*H*]-naphtho[2,1-*b*][1,4]oxazine], 9. This compound was synthesized from 9'-Hydroxy-1,3,3-trimethylspiro[indoline-2,3'-[3*H*]-naphtho[2,1-*b*][1,4]oxazine] using the literature procedure.[6] The pure compound, a pale yellow solid, was obtained after column chromatography (silica gel, diethyl ether/hexane, 1:1). Yield: 86%. ^{1}H NMR (200 MHz, d_6-acetone) δ 8.25 (d, J = 2.4 Hz, 1H), 7.77-7.89 (m, 3H), 7.12-7.23 (m, 3H), 7.03 (d, J = 8.9 Hz, 1H), 6.87 (m, 1H), 6.65 (d, J = 7.7 Hz, 1H), 2.76 (s, 3H, NCH_3), 2.69 (q, J = 7.5 Hz, 2H, propionyl-CH_2), 1.35 (s, 3H, *gem*-CH_3), 1.33 (s, 3H, *gem*-CH_3), 1.26 (t, J = 7.5 Hz, 3H, propionyl-CH_3) ppm. ^{13}C NMR (100 MHz, d_6-acetone) δ 173.4, 152.0, 151.1, 148.6, 145.6, 136.7, 132.6, 130.9, 130.2, 128.8, 128.1, 123.8, 122.3, 120.7, 120.6, 117.2, 113.7, 108.0, 99.8, 52.5, 29.8, 28.1, 25.7, 21.0, 9.4 ppm.

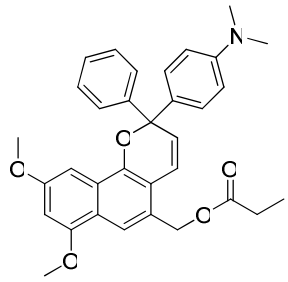


2,2-Bis(4-methoxyphenyl)-5-(2-propionyloxyethoxycarbonyl)-6-phenyl-[2*H*]-naphtho[1,2-*b*]pyran, 12. This compound was synthesized from 2,2-Bis(4-methoxyphenyl)-5-(2-hydroxyethoxycarbonyl)-6-phenyl-[2H]-naphtho[1,2-b]pyran using the literature procedure.[6] Purification by column chromatography (silica gel, ethyl acetate/hexane, 3:2), gave the pure product as a pink solid. Yield: 97%. ^{1}H NMR

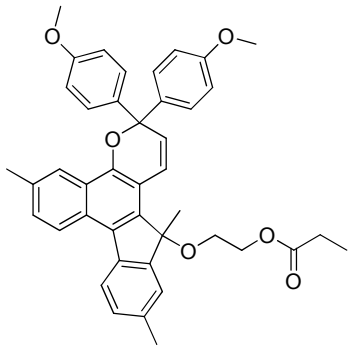
(200 MHz, d_6-acetone) δ 8.46 (m, 1H), 7.57-7.65 (m, 1H), 7.45-7.52 (m, 9H), 7.28-7.33 (m, 2H), 6.92 (d, *J* = 8.9 Hz, 4H), 6.84 (d, *J* = 10 Hz, 1H, pyran-CH), 6.44 (d, *J* = 10 Hz, 1H, pyran-CH), 4.19 (m, 2H), 3.98 (m, 2H), 3.77 (s, 6H, CH_3O), 2.31 (q, *J* = 7.5 Hz, 2H, propionyl-CH_2), 1.07 (t, *J* = 7.5 Hz, 3H, propionyl-CH_3) ppm. ^{13}C NMR (50MHz, d_6-acetone) δ 175.1, 169.4, 161.0, 149.2, 139.6, 138.8, 134.5, 132.4, 132.2, 131.3, 130.6, 129.9, 129.8, 129.4, 129.1, 128.7, 128.5, 126.9, 123.8, 122.2, 115.3, 114.2, 84.7, 64.5, 63.4, 56.5, 28.6, 10.3 ppm. MS (EI): *m/z* 614.3 [M^+]; MS (HR, EI): *m/z* 614.2304 ($C_{39}H_{34}O_7$ requires 614.2305).



3,3-Bis(4-methoxyphenyl)-13-propionyloxy-indeno[2,1-*f*]naphtho[1,2-*b*]pyran, 15. This compound was synthesized from 3,3-Bis(4-methoxyphenyl)-13-hydroxy-indeno[2,1-*f*]naphtho[1,2-*b*]pyran using the literature procedure.[6] The pure product was obtained by crystallization from diethyl ether/hexane. ^{1}H NMR (200 MHz, $CDCl_3$) δ 8.41-8.54 (m, 2H), 8.08 (d, *J* = 7.8 Hz, 1H), 7.38-7.62 (m, 8H), 7.19-7.26 (m, 1H), 7.04 (s, 1H), 6.77-6.87 (m, 5H), 6.23 (d, *J* = 9.9 Hz, 1H, pyran-CH), 3.76 (s, 6H, CH_3O), 2.49 (q, *J* = 7.6 Hz, 2H, propionyl-CH_2), 1.26 (t, *J* = 7.6 Hz, 3H, propionyl-CH_3) ppm. ^{13}C NMR (50 MHz, $CDCl_3$) δ 175.0, 158.9, 148.3, 142.7, 142.3, 137.1, 137.0, 136.6, 129.7, 129.4, 129.2, 129.1, 128.2, 128.1, 127.3, 126.0, 125.8, 125.6, 125.4, 123.8, 123.3, 122.0, 119.8, 113.5, 113.4, 113.1, 83.0, 73.8, 55.2, 28.0, 9.4 ppm. MS (EI): *m/z* 554.3 [M^+]; MS (HR, EI): *m/z* 554.2085 ($C_{37}H_{30}O_5$ requires 554.2093).

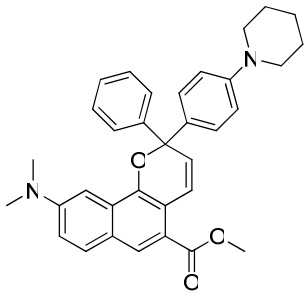


2-(4-Dimethylaminophenyl)-2-phenyl-5-propionyloxymethyl-7,9-methoxy-[2*H*]-naphtho[1,2-*b*]pyran, 18. This compound was synthesized from 2-(4-Dimethylaminophenyl)-2-phenyl-5-hydroxymethyl-7,9-methoxy-[2*H*]-naphtho[1,2-*b*]pyran using the literature procedure.[6] Yield: 96%. ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.47-7.52 (m, 2H), 7.17-7.38 (m, 6H), 6.87 (d, *J* = 10.0 Hz, 1H, pyran-CH), 6.74 (br s, 2H), 6.46 (d, *J* = 2.0 Hz, 1H), 6.19 (d, *J* = 10.0 Hz, 1H, pyran-CH), 5.26 (s, 2H, $ArCH_2$), 3.93 (s, 3H, CH_3O), 3.92 (s, 3H, CH_3O), 2.93 (s, 6H, $N(CH_3)_2$), 2.36 (q, *J* = 8.0 Hz, 2H, propionyl-CH_2), 1.14 (t, *J* = 8.0 Hz, 3H, propionyl-CH_3) ppm. ^{13}C NMR (200 MHz, $CDCl_3$) δ 174.2, 158.5, 156.5, 147.3, 145.3, 128.7, 128.1, 127.9, 127.2, 126.7, 126.5, 125.9, 121.7, 120.2, 116.1, 115.8, 98.2, 92.5, 82.5, 64.6, 55.5, 27.7, 9.1 ppm.

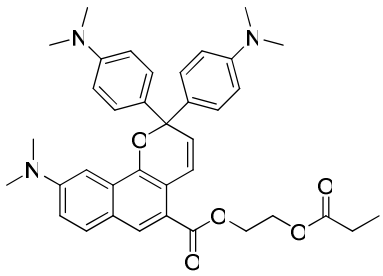


3,3-Bis(4-methoxyphenyl)-6,11,13-trimethyl-13-(2-propionyloxyethoxy)-indeno[2,1-*f*] naphtho[1,2-*b*]pyran, 21. This compound was synthesized from 3,3-Bis(4-methoxyphenyl)-6,11,13-trimethyl-13-(2-hydroxyethoxy)-indeno[2,1-*f*] naphtho[1,2-*b*]pyran using the literature procedure.[6] Yield: 71%. ^{1}H NMR (200 MHz, d_6-acetone) δ 8.52 (d, *J* = 8.7 Hz, 1H), 8.25 (s, 1H), 8.06 (d, *J* = 8 Hz, 1H), 7.55-7.44 (m, 6H), 7.35 (s, 1H), 7.25 (d, *J* = 7.8 Hz, 1H), 6.93 (d, *J* = 9 Hz, 2H), 6.86 (d, *J* = 9

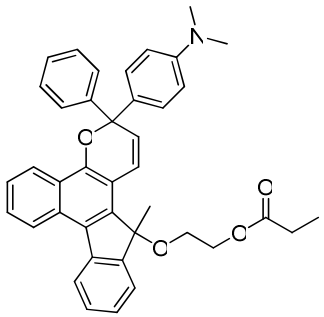
Hz, 2H), 6.40 (d, *J* = 9.9 Hz, 1H), 4.07 (m, 2H, $COOCH_2$), 3.78 (s, 3H, CH_3O), 3.73 (s, 3H, CH_3O), 3.02 (m, 2H, $COOCH_2CH_2O$), 2.55 (s, 3H, $ArCH_3$), 2.42 (s, 3H, $ArCH_3$), 2.30 (q, *J* = 7.6 Hz, 2H, propionyl-CH_2), 1.70 (s, 3H, indeno-CH_3), 1.04 (t, *J* = 7.6 Hz, 3H, propionyl-CH_3) ppm.



2-Phenyl-2-(4-piperidinophenyl)-5-methoxycarbonyl-9-dimethylamino-2*H*-naphtho[1,2-*b*]pyran, 27. This compound is commercially available from James Robinson Ltd.



2,2-Bis(4-dimethylaminophenyl)-5-(2-propionyloxyethoxycarbonyl)-9-dimethylamino-2*H*-naphtho[1,2-*b*]pyran, 30. This compound was synthesized from 2,2-Bis(4-dimethylaminophenyl)-5-(2-hydroxyethoxycarbonyl)-9-dimethylamino-2*H*-naphtho[1,2-*b*]pyran using the literature procedure.[6] The pure compound was obtained after column chromatography (silica gel, CH_2Cl_2/diethyl ether, 10:1). Yield: 89%. ^1H NMR (400 MHz, d_6-acetone) δ 7.99 (s, 1H), 7.71 (d, *J* = 9.1 Hz, 1H), 7.66 (d, *J* = 10 Hz, 1H), 7.36 (m, 5H), 7.21 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.65 (d, *J* = 8.9 Hz, 4H), 6.28 (d, *J* = 10 Hz, 1H), 4.50 (m, 2H, CH_2O), 4.44 (m, 2H, CH_2O), 3.10 (s, 6H, naphthyl-$N(CH_3)_2$), 2.86 (s, 12H, *gem*-Ph $N(CH_3)_2$), 2.37 (q, *J* = 7.6 Hz, 2H, propionyl-CH_2), 1.10 (t, *J* = 7.5 Hz, 3H, propionyl-CH_3) ppm.



3-(4-Dimethylaminophenyl)-3-phenyl-13-methyl-13-(2-(propionyloxy)ethoxy)-indeno[2,1-*f*]naphtho[1,2-*b*]pyran, 36. This compound was synthesized from 3-(4-Dimethylaminophenyl)-3-phenyl-13-methyl-13-(2-hydroxyethoxy)-indeno[2,1-*f*]naphtho[1,2-*b*]pyran using the literature procedure.[6] The pure compound was obtained after column chromatography (silica gel, EtOAc/hexane, 1:2). ^{1}H NMR (400 MHz, d_6-acetone) δ 8.66 (d, J = 8.4 Hz, 1H), 8.49 (d, J = 8.4 Hz, 1H), 8.23 (d, J = 7.8 Hz, 1H), 7.67-7.51 (m, 6H), 7.47-7.21 (m, 7H), 6.70 (d, J = Hz, 1H), 6.63 (d, J = 8.9 Hz, 1H), 6.47 and 6.41 (2 × d, J = 9.9 Hz, 1H, pyran-CH), 4.10 (m, 2H), 3.05 (m, 2H), 2.89 (s, 3H, NCH_3), 2.84 (s, 3H, NCH_3), 2.33 and 2.27 (2 × q, J = 7.5 Hz, 2H, $COCH_2$), 1.74 and 1.72 (2 × s, 3H, indeno-CH_3), 1.06 and 1.00 (2 × t, J = 7.5 Hz, 3H, propionyl-CH_3) ppm.

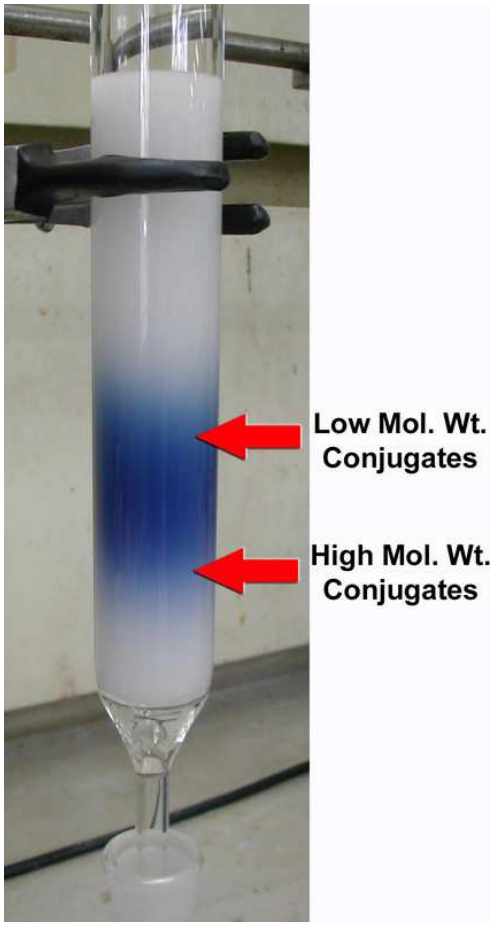
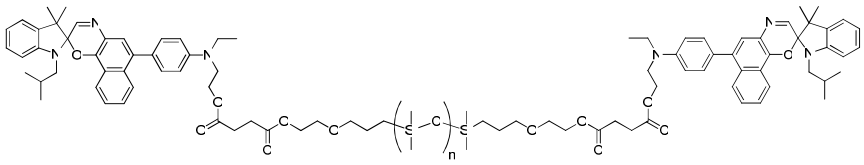
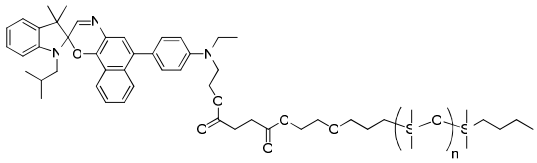


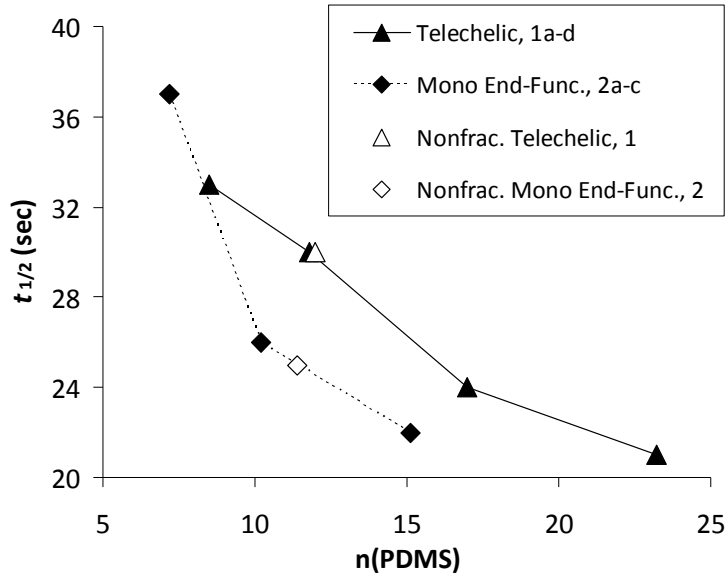
Figure S1: Fractionation of photochromic PDMS conjugates by silica gel column chromatography gives fractions having a range of average molecular weights.



1a-d



2a-c



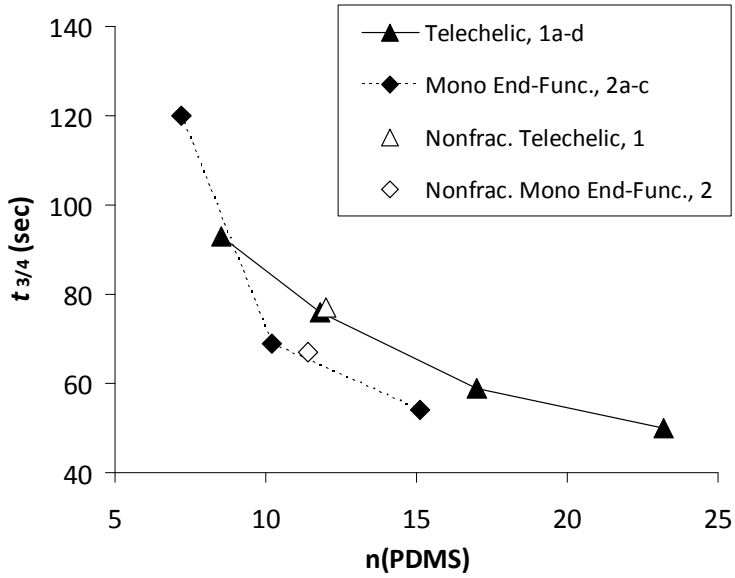
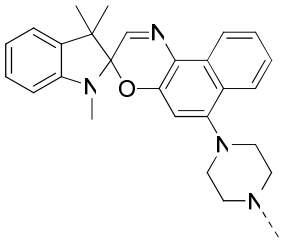
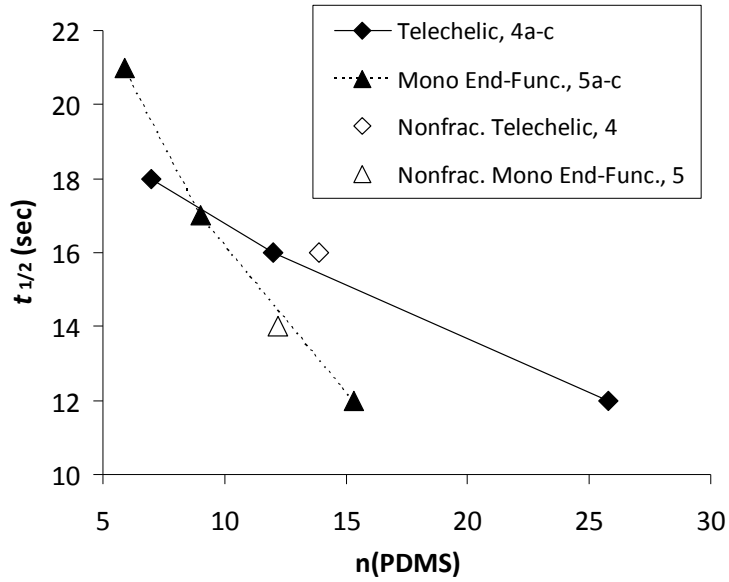


Figure S2: Plots of $t_{1/2}$ and $t_{3/4}$ versus n_{PDMS} for spirooxazine-PDMS conjugates **1**, **1a-d** (telechelic conjugates) and **2**, **2a-c** (mono end-functionalized conjugates).





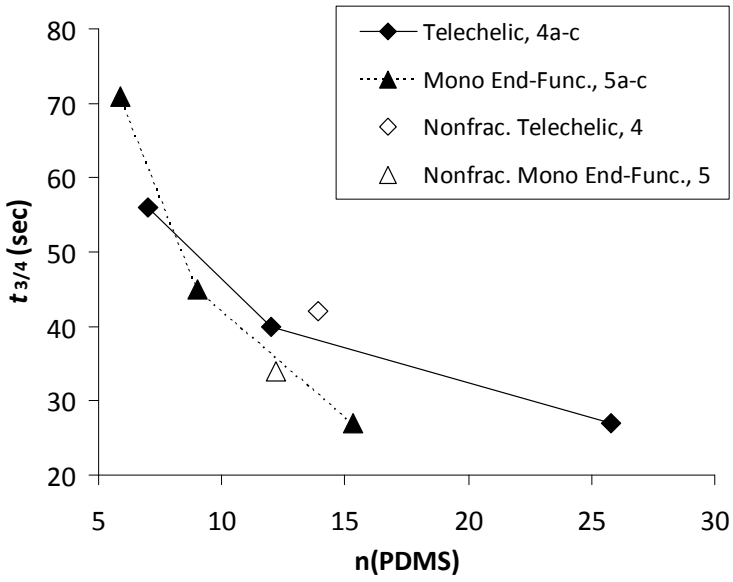
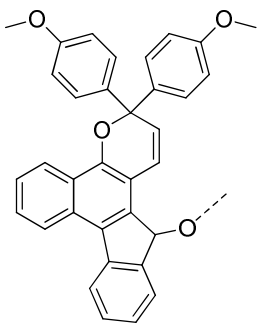
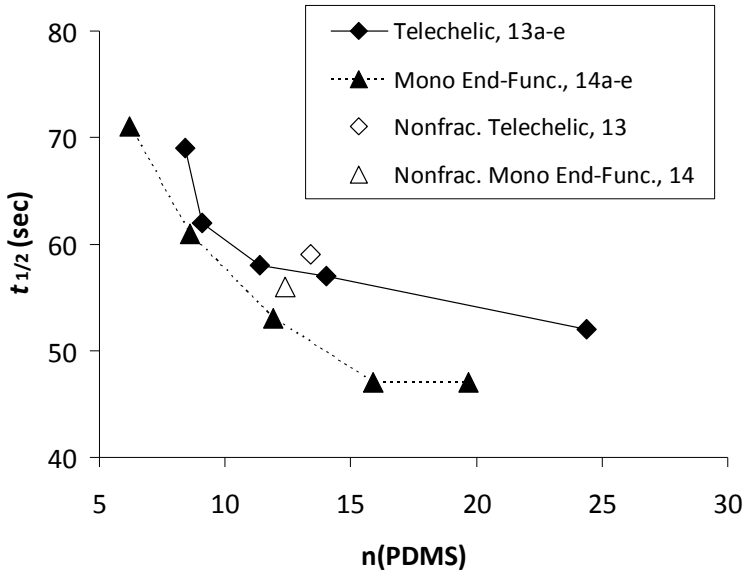


Figure S3: Plots of $t_{1/2}$ and $t_{3/4}$ versus n_{PDMS} for poly(dimethylsiloxane) conjugated 6'-Piperazine-1,3,3-trimethylspiro[indoline-2,3'-[3*H*] naphtho[2,1-*b*][1,4]oxazine.





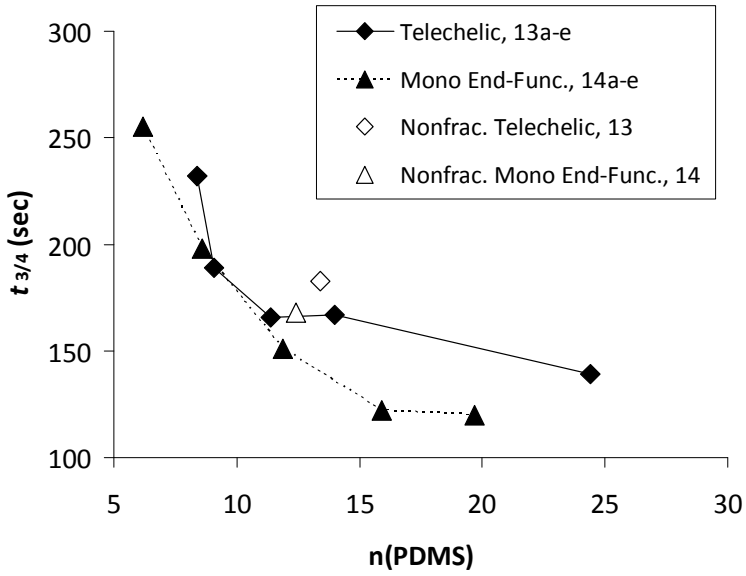
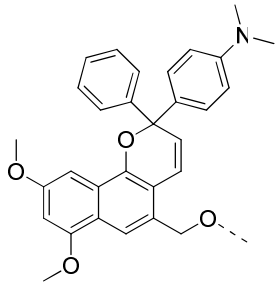
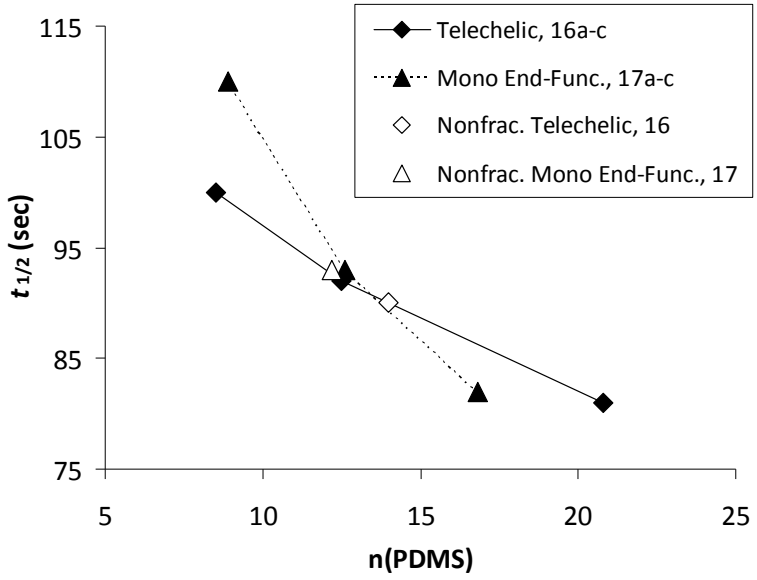


Figure S4: Plots of $t_{1/2}$ and $t_{3/4}$ versus n_{PDMS} for poly(dimethylsiloxane) conjugated 3,3-Bis(4-methoxyphenyl)-13-hydroxy-indeno[2,1-*f*]naphtho[1,2-*b*]pyran.





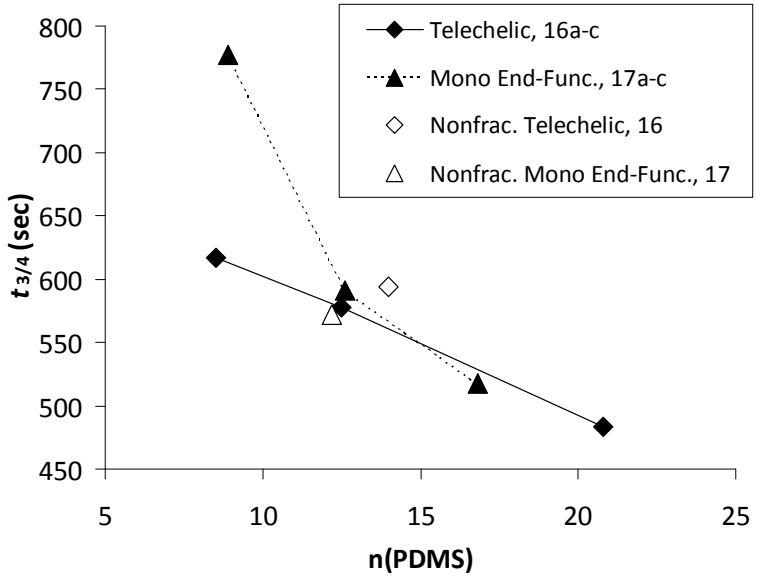


Figure S5: Plots of $t_{1/2}$ and $t_{3/4}$ versus n_{PDMS} for poly(dimethylsiloxane) conjugated 2-(4-Dimethylaminophenyl)-2-phenyl-5-hydroxymethyl-7,9-methoxy-[2*H*]-naphtho[1,2-*b*]pyran.

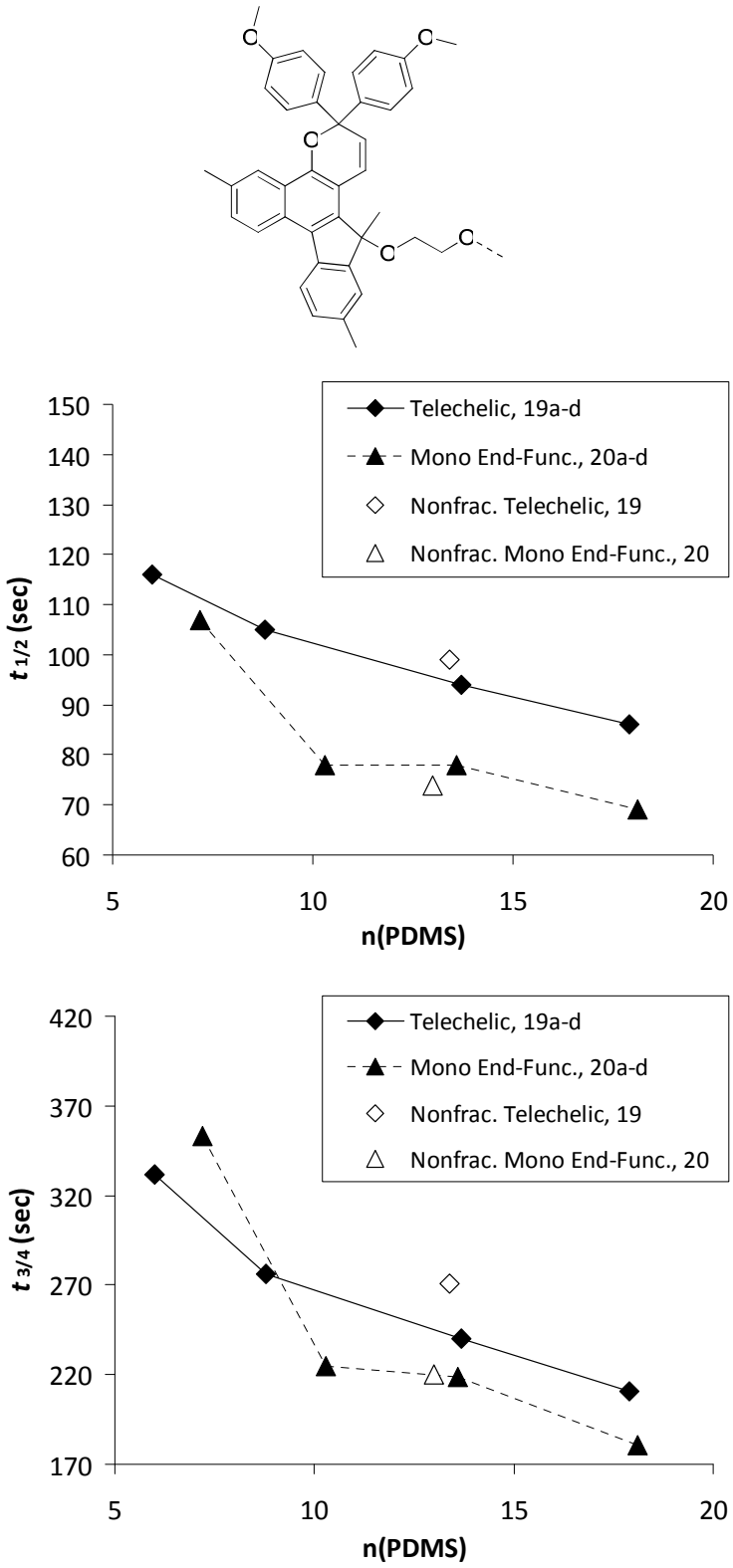
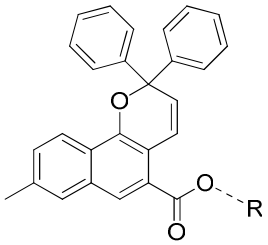
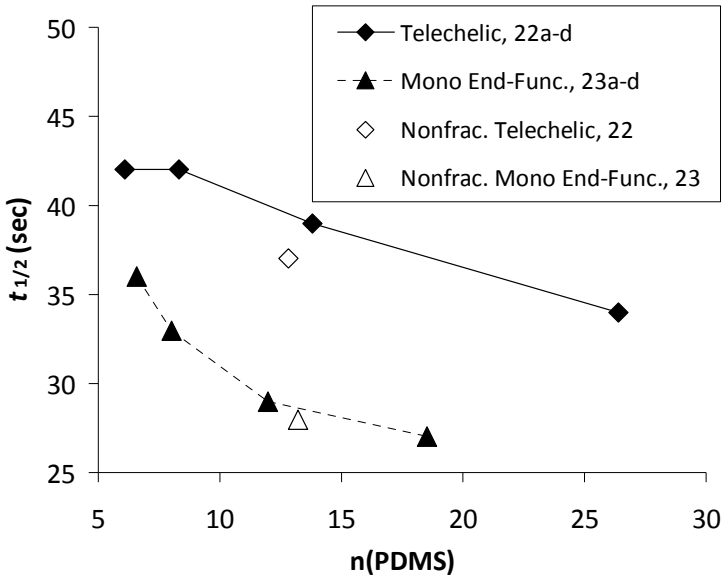


Figure S6: Plots of $t_{1/2}$ and $t_{3/4}$ versus n_{PDMS} for poly(dimethylsiloxane) conjugated 3,3-Bis(4-methoxyphenyl)-6,11,13-trimethyl-13-hydroxy-indeno[2,1-*f*]naphtho[1,2-*b*]pyran.





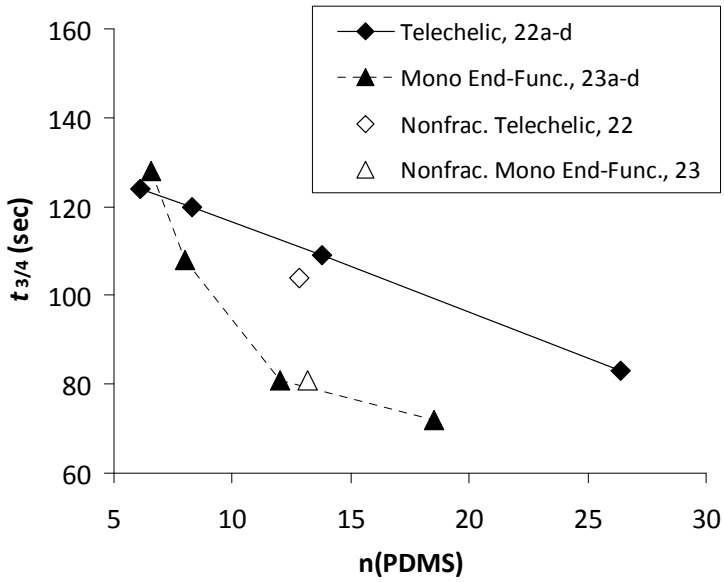


Figure S7: Plots of $t_{1/2}$ and $t_{3/4}$ versus n_{PDMS} for poly(dimethylsiloxane) conjugated 2,2-Diphenyl-5-carboxylic acid-8-methyl-2*H*-naphtho[1,2-*b*]pyran.

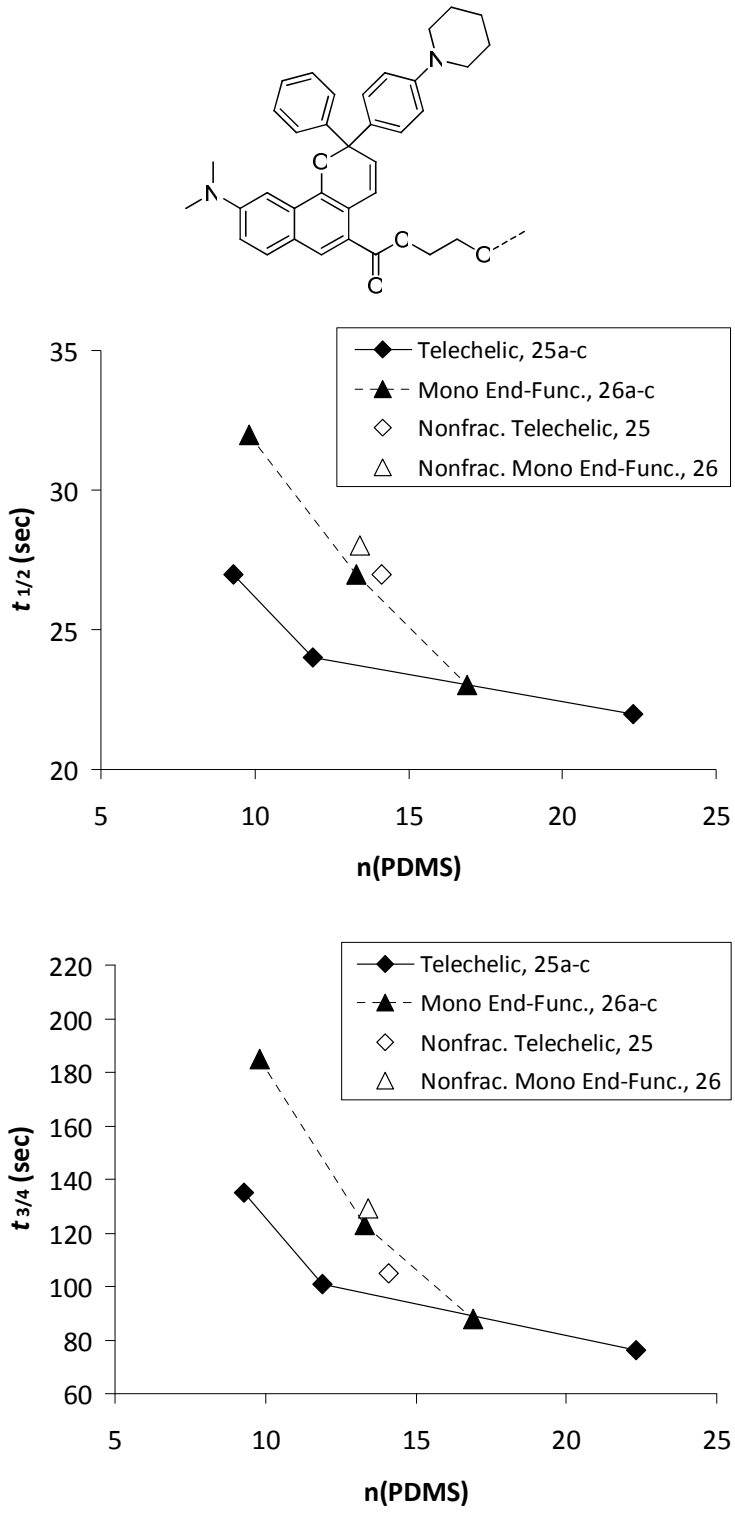


Figure S8: Plots of $t_{1/2}$ and $t_{3/4}$ versus n_{PDMS} for poly(dimethylsiloxane) conjugated 2-Phenyl-2-(4-piperidinophenyl)-5-(2-hydroxyethoxycarbonyl)-9-dimethylamino-2*H*-naphtho[1,2-*b*]pyran.

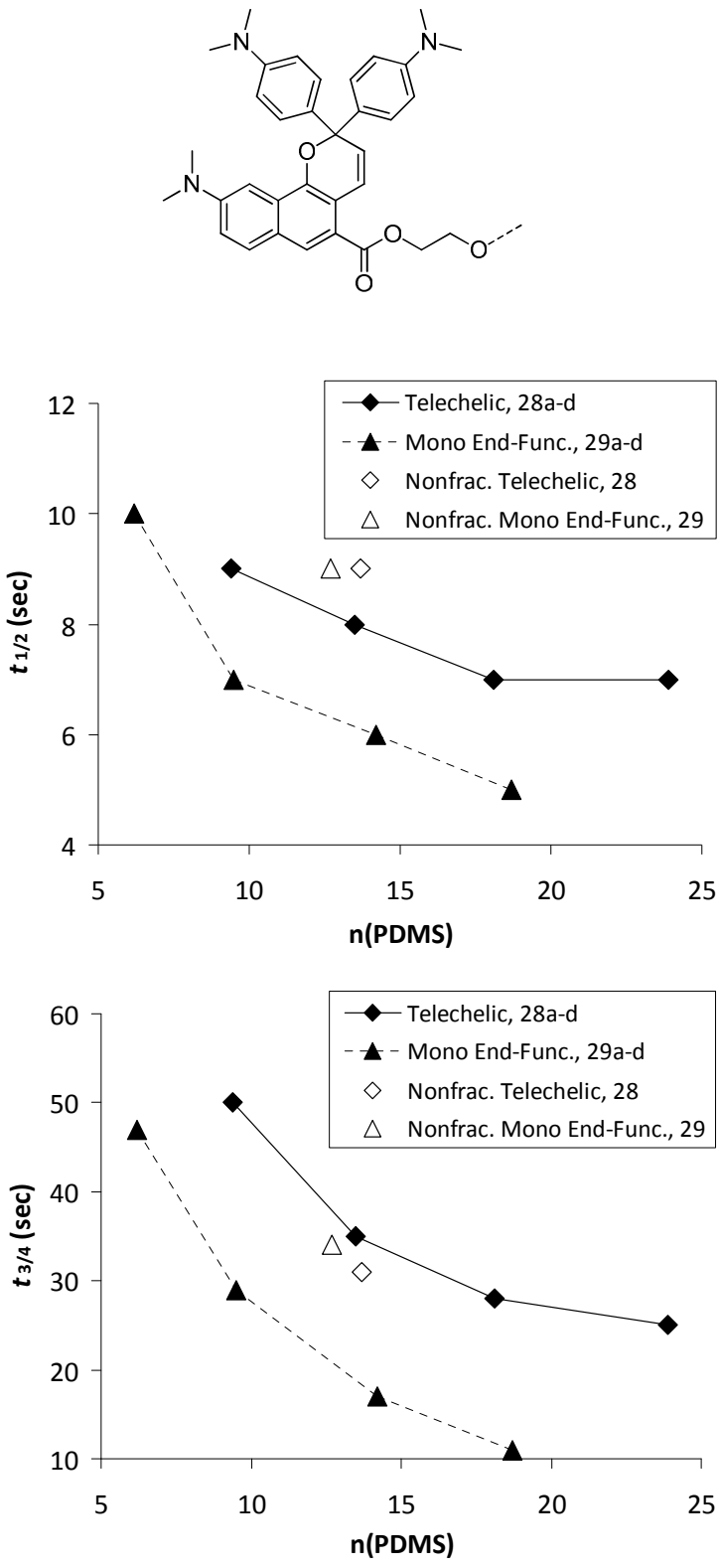
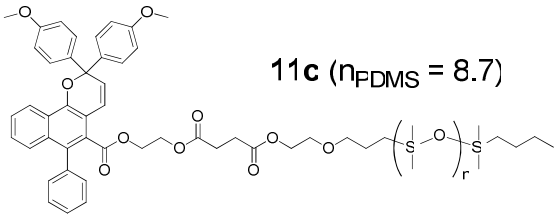
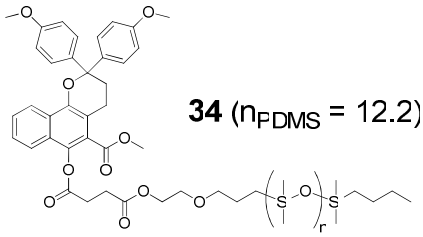


Figure S9: Plots of $t_{1/2}$ and $t_{3/4}$ versus n_{PDMS} for poly(dimethylsiloxane) conjugated 2,2-Bis(4-dimethylaminophenyl)-5-(2-hydroxyethoxycarbonyl)-9-dimethylamino-2*H*-naphtho[1,2-*b*]pyran.

Table S1: Decoloration performance of photochromic conjugate **11c** (n_{PDMS} = 8.7) in test lens matrix (EBPDMA:PEGDMA) containing varying amounts of non-photochromic model compound **34** (n_{PDMS} = 12.2)





Entry	Photochromic conjugate, **11c** (molar equiv.)[a]	Non-Photochromic conjugate, **34** (molar equiv.)	A_0[b]	$t_{1/2}$ (sec)	$t_{3/4}$ (sec)
1	0.25	0	0.25	38	178
2	0.25	1	0.26	38	170
3	0.25	2	0.25	36	157
4	0.25	3	0.24	39	167
5	1	0	0.85	37	171
6	1	0.5	0.73	37	165
7	1	1	0.81	36	165
8	1	2	0.76	38	164

[a] Conjugate concentration (1 molar equiv.) = 1.50×10^{-7} mol/g

[b] Absorption at 1000 sec UV irradiation.

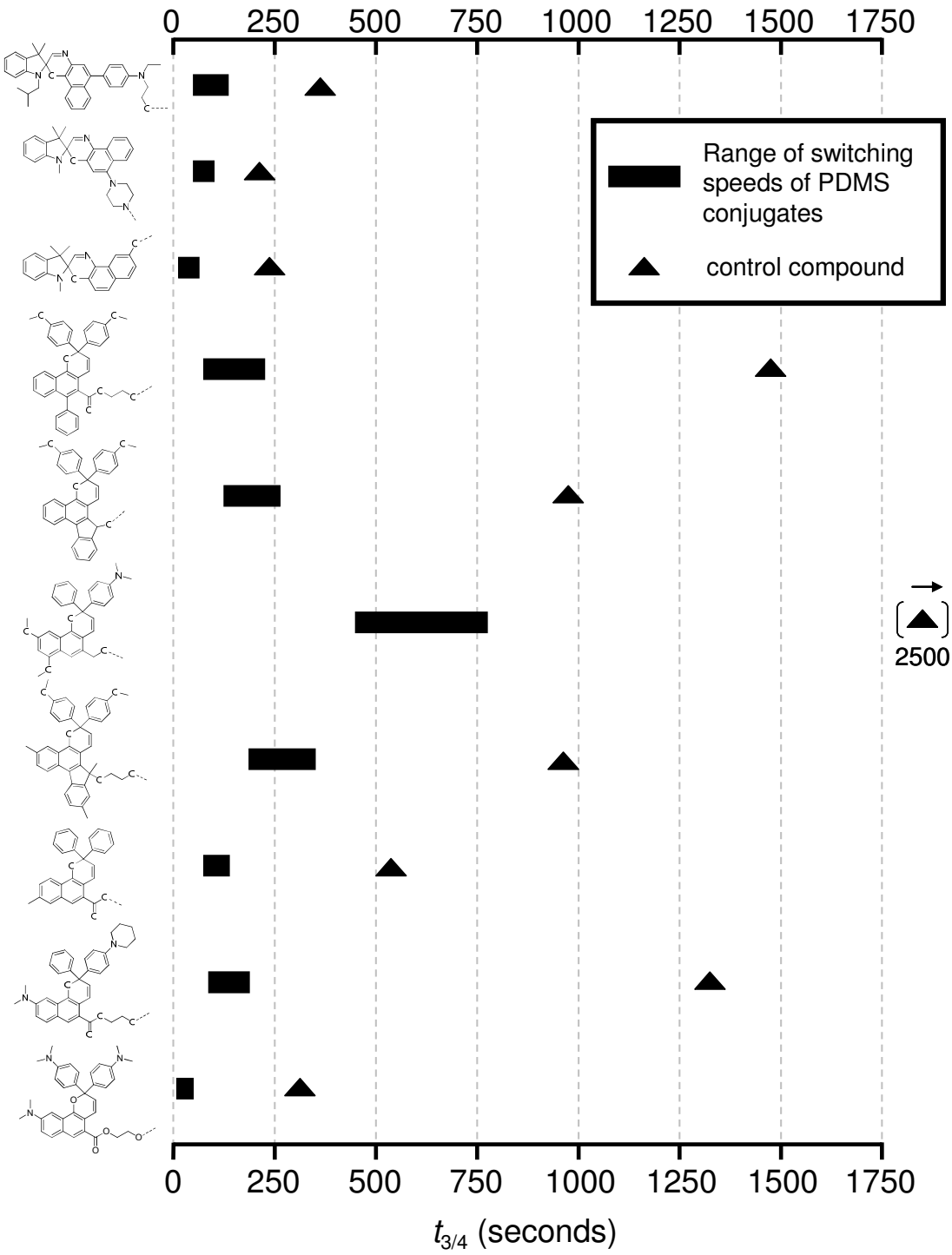


Figure S10: Plots of the range of $t_{3/4}$ values of each photochromic dye conjugate system tested in a rigid polymer matrix, indicating potential for synchronization in multi-dye systems where overlap is observed.

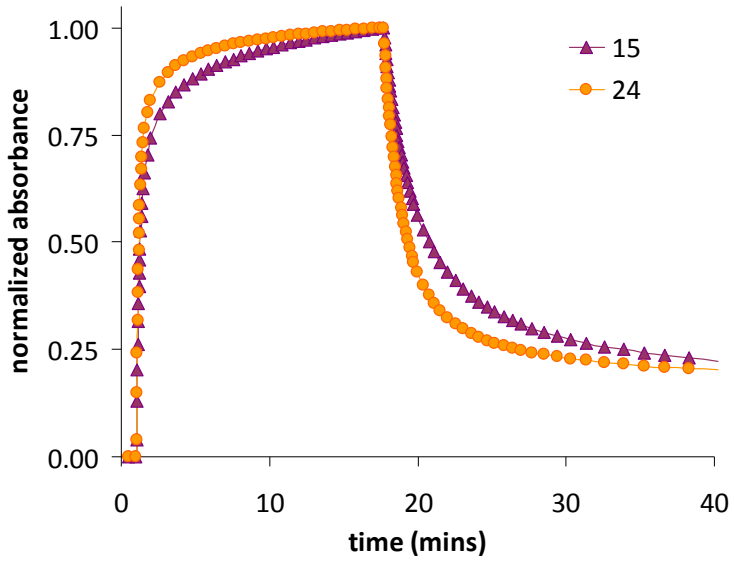


Figure S11: Superimposed kinetic profiles of coloration (60-1000 sec) and decoloration (1000 sec onwards) of non-synchronized, non-PDMS conjugated control dyes **15** and **24** within a test lens matrix formulation (EBPDMA:PEGDMA, 4:1).

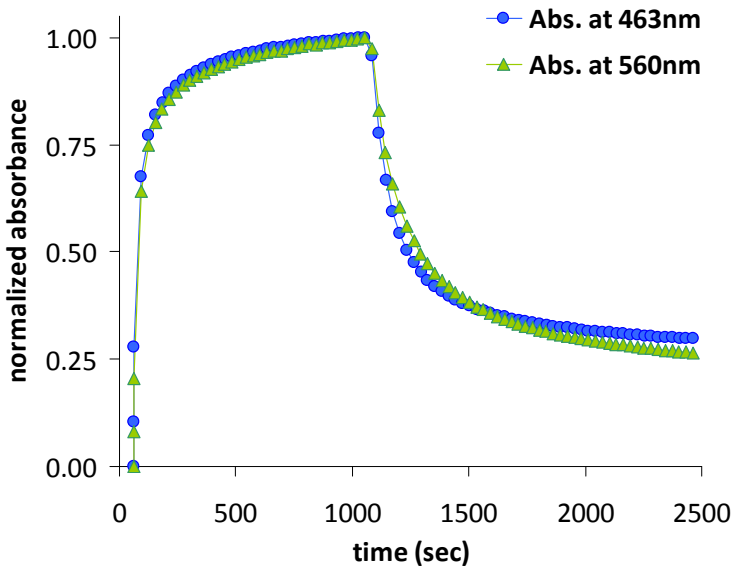
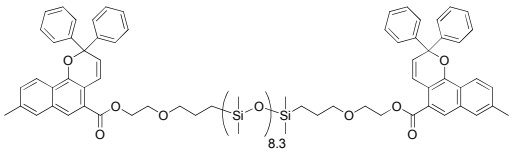
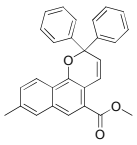


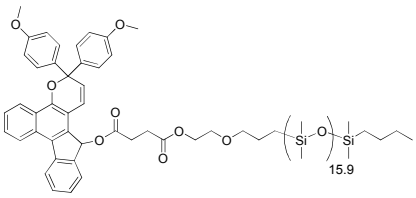
Figure S12: Monitoring of color development and decoloration in the dark of lens samples containing combined non-synchronized, non-PDMS conjugated, control dyes **15** and **24** (slow and uneven color fade). Absorbance readings taken at 560 and 463 nm (λ_{max} values of the individual dye components, respectively) from visible spectrum recorded at 30 second intervals.



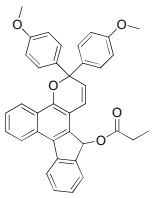
22c, Orange (λ_{max} = 463 nm)
$t_{1/2}$ = 42 sec, $t_{3/4}$ = 120 sec



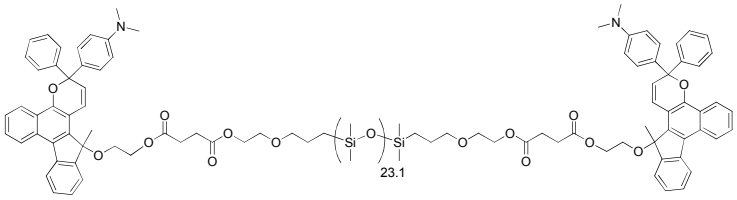
24, Orange (λ_{max} = 463 nm)
$t_{1/2}$ = 100 sec, $t_{3/4}$ = 547 sec



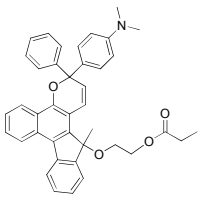
14b, Purple (λ_{max} = 560 nm)
$t_{1/2}$ = 47 sec, $t_{3/4}$ = 122 sec



15, Purple (λ_{max} = 560 nm)
$t_{1/2}$ = 186 sec, $t_{3/4}$ = 978 sec



35b, Blue (λ_{max} = 615 nm)
$t_{1/2}$ = 43 sec, $t_{3/4}$ = 115 sec



36, Blue (λ_{max} = 615 nm)
$t_{1/2}$ = 114 sec, $t_{3/4}$ = 616 sec

Figure S13: Fade speed synchronized photochromic dye-PDMS conjugates used to produce grey colored lens with fast coloration and decoloration performance (left). Corresponding control dyes (right).

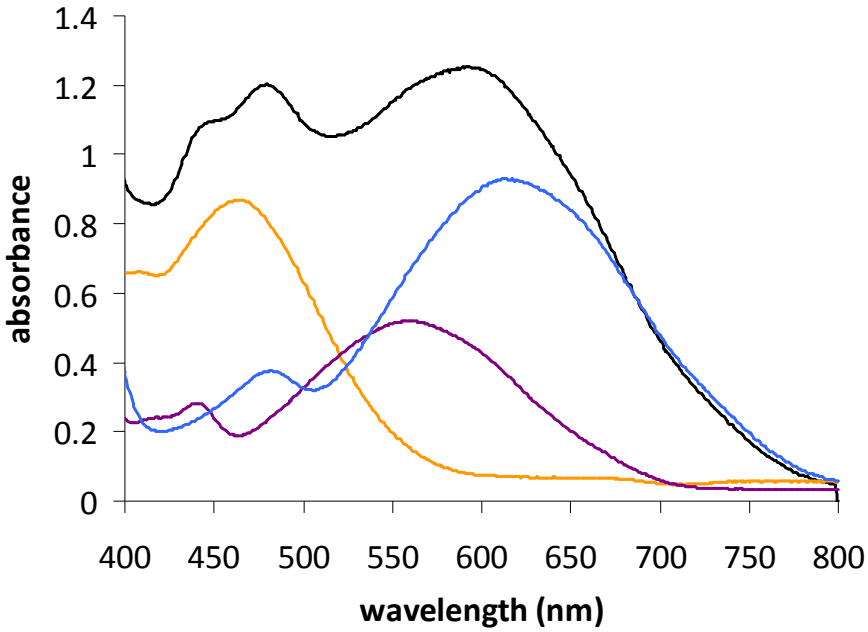


Figure S14: Visible spectrum of grey lens containing 3 synchronized dyes at 1000 sec UV (350-400 nm) irradiation (black line); Visible spectra of the individual dye components (orange, purple and blue lines).

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