

# Triplet Pathways in Diarylethene Photochromism. Photophysical and Computational Study of Dyads Containing Ruthenium(II) Polypyridine and 1,2-bis(2-methylbenzothiophene-3-yl)maleimide and Units.

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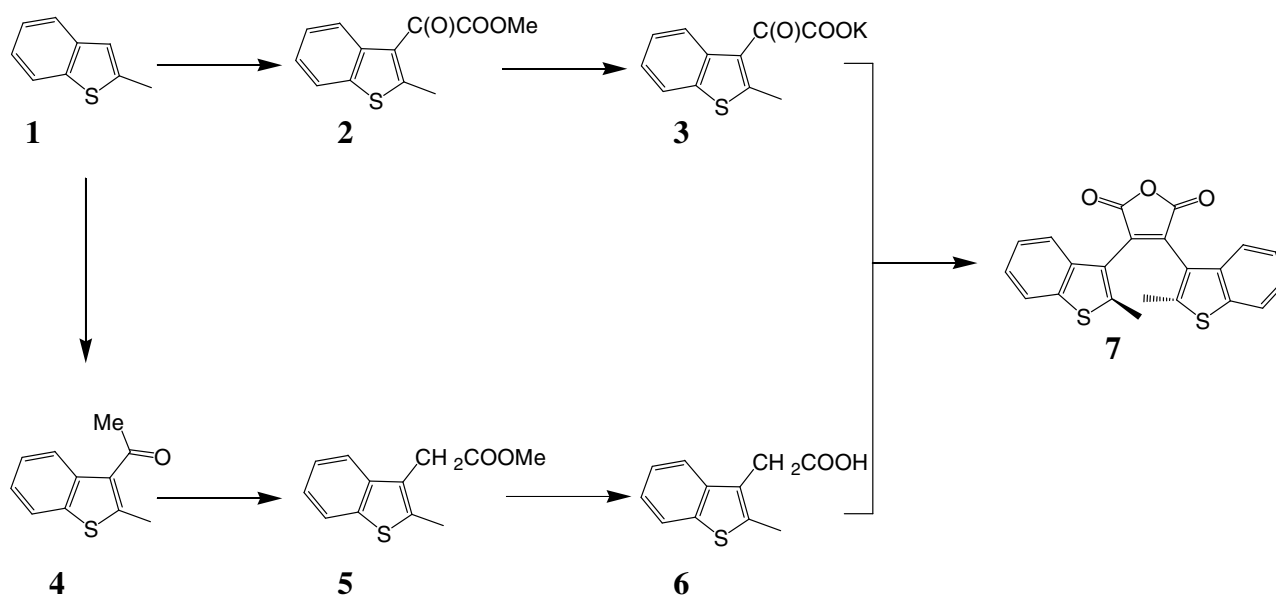
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## Supporting Information

## Syntheses.

The dyads **Ru-DAE** and **Ru-CH<sub>2</sub>-DAE** have been obtained by a general procedure that consists in the preparation of the phenanthroline type ligand containing the photochromic DAE moiety and the subsequent coordination of this ligand to the Ru(II) center. The key step in the synthesis of both photochromic ligands involves the preparation of the 3,4-bis[2-methyl-benzothienyl]maleic anhydride obtained by a Perkin reaction,<sup>1</sup> as indicated in Scheme 1 (see experimental section for synthetic details).

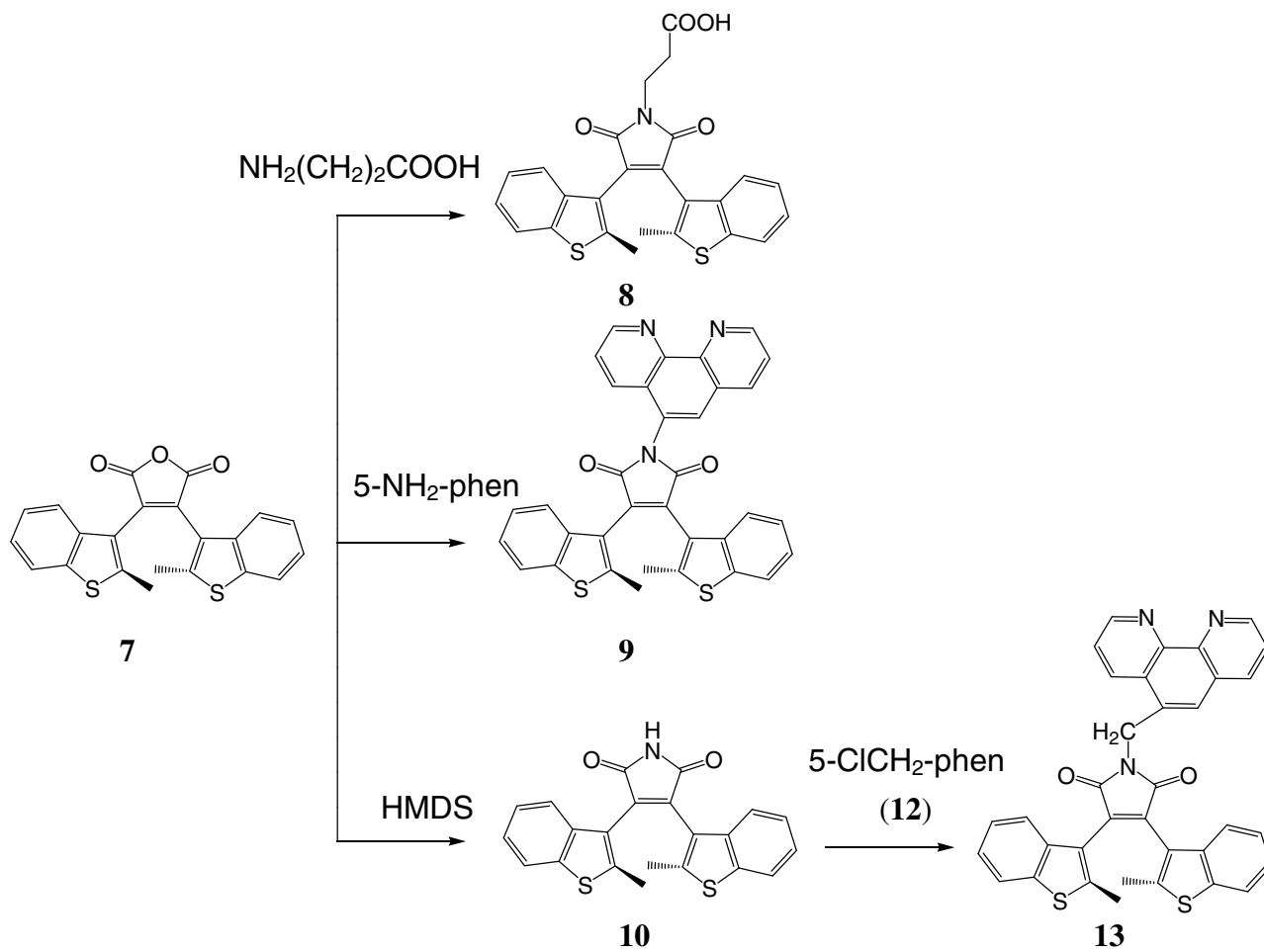
**Scheme 1.** Synthesis of the maleic anhydride (**7**).



The **DAE** photochromic unit (**8**) and the ligand (**9**) were obtained directly by reaction of maleic anhydride (**7**) with the primary amines  $\beta$ -alanine and 5-amino-[1,10]-phenanthroline respectively (Scheme 2). The ligand (**13**), where the diarylethene unit is connected through a methylenic spacer

to the phenanthroline, has been prepared by the nucleophilic substitution of the maleimide (**10**) to the chloromethyl derivate (**12**) (Scheme 2).

**Scheme 2.** Synthesis of the photochromic maleimides.



The dyads **Ru-DAE** and **Ru-CH<sub>2</sub>-DAE** were then straightforwardly prepared by reaction of ligands **9** and **12** with the  $\text{Ru}(\text{bpy})_2\text{Cl}_2$  complex.

**Methyl 2-(2-methylbenzo[b]thiophen-3-yl)-2-oxoacetate (2).** To a cooled (0°C) and well stirred mixture of AlCl<sub>3</sub> (3.63 g, 27.2 mmol) and CH<sub>2</sub>Cl<sub>2</sub> (40 ml) were added methyl-chlorooxoacetate (1.25 ml, 13.6 mmol) and a solution of 2-methyl-benzo[b]thiophene (**1**) (1 g, 6.8 mmol) in the minimum amount of CH<sub>2</sub>Cl<sub>2</sub>. The mixture were stirred at room temperature for 2 hr and quenched in a mixture of water/ice. The crude mixture were extracted with CH<sub>2</sub>Cl<sub>2</sub> and the organic phase were washed with a saturated solution of NaHCO<sub>3</sub>aq. The organic layers were dried over anhydrous sodium sulphate and taken to drieness under vacuo to give 1.46 g (92%) of (**2**) as a brown oil.

<sup>1</sup>H NMR (δ/ppm, CDCl<sub>3</sub>) 2.78 (3H, s, CH<sub>3</sub>), 4.00 (3H, s, CH<sub>3</sub>), 7.30-7.50 (2H, m), 7.80 (1H, d J = 6.98 Hz), 8.30 (1H, d J = 6.98 Hz). IR: 1650, 1735 cm<sup>-1</sup>.

**Potassium 2-(2-methylbenzo[b]thiophen-3-yl)-2-oxoacetate (3).** A solution of (**2**) (0.79 g, 3.4mmol ) in ethanol (10 ml) were treated with KOH (0.13 g, 3.4mmol). The solution were stirred at room temperature for 4 hr and the solvent were removed under reduced pressure. The white solid (**3**) were dried to 40°C overnight.

**1-(2-methylbenzo[b]thiophen-3-yl)ethanone (4).** A mixture of (**1**) (0.51 g, 3.4 mmol) AlCl<sub>3</sub> (1.2 g, 8.5 mmol), acethyl-chloride 0.3 ml (4.08 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (15 ml) was treated in a similar manner as described for the synthesis of (**2**). The crude product was purified over SiO<sub>2</sub> (cyclohexane/ethyl acetate 8:1) to give 0.43 g (67%) of a white solid (**4**).

<sup>1</sup>H NMR (δ/ppm, CDCl<sub>3</sub>) 2.64 (3H, s), 7.25÷7.45 (2H, m), 7.78 (1H, d J = 6.98 Hz), 8.20 (1H, d J: 6.98 Hz). IR: 1650 cm<sup>-1</sup>.

**Methyl 2-(2-methylbenzo[b]thiophen-3-yl) acetate (5).** A mixture of (**4**) (0.43 g, 2.3 mmol), methanol (10 ml), thallium (III) trinitrate trihydrate (TTN, 1.02 g, 2.76 mmol) and 65% HClO<sub>4</sub> (1.15 ml) were stirred at room temperature for 16 hr following a published method.<sup>ii</sup> The mixture was concentrated under vacuo (40°C), washed with water and extracted with chloroform. The organic phase was dried over anhydrous sodium sulphate and the solvent was evaporated. The crude mixture was purified with a flash chromatography on SiO<sub>2</sub> (cyclohexane/ethyl acetate 8:1) to give (**5**) (0.46 g, 90 %) as a yellow oil.

$^1\text{H}$  NMR ( $\delta$ /ppm,  $\text{CDCl}_3$ ) 2.59 (3H, s), 3.63 (3H, s), 3.80 (2H, s), 7.23 ÷ 7.41 (2H, m), 7.63 (1H, d J: 6.98 Hz), 7.79 (1H, d J: 6.98 Hz). IR: 1725  $\text{cm}^{-1}$ .

**2-(2-methylbenzo[b]thiophen-3-yl) acetic acid (6).** A solution of the ester (**5**) (0.62 g (2.8 mmol) in ethanol (8 ml) was treated at room temperature with NaOH (0.17 g, 4.2 mmol) for 4 hr. The solution was concentrated under vacuo, water was added. The water solution was first extracted with ether and finally acidified to pH = 1 with HCl. The white precipitate was filtrated and dried (40°C) to give 0.56 g (100%) of the acid (**6**).

$^1\text{H}$  NMR ( $\delta$ /ppm,  $\text{CDCl}_3$ ) 2.55 (3H, s), 3.80 (2H, s), 7.20 ÷ 7.40 (2H, m), 7.65 (1H, d J: 6.98 Hz), 7.85 (1H, d J: 6.98 Hz).

**3,4-Bis(2-methylbenzo[b]thiophen-3-yl)furan-2,5-dione (7).** A mixture of the acid (**6**) (0.5 g, 2.4 mmol), the potassium salt (**3**) (0.6 g, 2.4 mmol) and acetic anhydride (4.6 ml) was stirred and heated to 110°C for 4 hr. The mixture was cooled to room temperature and quenched by adding water (15 ml). The organic phase was extracted with ether, dried over anhydrous sodium sulphate and the solvent was evaporated under vacuum. The crude product was purified over silica gel (cyclohexane/ethyl acetate 3:1) to yield the maleic anhydride (**7**) as an orange solid (0.7 g, 75%).

$^1\text{H}$  NMR ( $\delta$ /ppm,  $\text{CDCl}_3$ ) 2.11 (s, 3H), 2.29 (s, 3H), 7.10÷7.80 (m, 8H). IR (KBr) 1710  $\text{cm}^{-1}$  (CO). ESI m/z: 390  $[\text{M}+\text{H}]^+$ .

**(3,4-bis(2-methylbenzo[b]thiophen-3-yl)-1-(propanoic acid-3-yl)-1H-pyrrole-2,5-dione (8, DAE).** A mixture of the maleic anhydride (**7**) (0.5 g, 1.3 mmol) and  $\beta$ -alanine (0.14 g, 1.54 mmol) was heated with an oil bath to 150°C for 1 hr. The solid was purified with a flash chromatography (silica gel, cyclohexane/ethyl acetate 2:1) to give 0.6 g (100%) of the maleimide (**8**).

$^1\text{H}$  NMR ( $\delta$ /ppm,  $\text{CDCl}_3$ ) 1.98 (3H, s), 2.37 (3H, s), 2.95 (2H, m), 4.1 (2H, m), 7.00÷7.80 (8H, m). FT-IR (KBr): 1703  $\text{cm}^{-1}$ . ESI m/z: 462  $[\text{M}+\text{H}]^+$ , 484  $[\text{M}+\text{Na}]^+$ , 500  $[\text{M}+\text{K}]^+$ .

**3,4-bis(2-methylbenzo[b]thiophen-3-yl)-1-(1,10-phenanthroline-5-yl)-1H-pyrrole-2,5-dione (9, phen-DAE).** A mixture of (**7**) (0.1 g, 0.25mmol) and 5-amino-[1,10] phenanthroline (0.05 g,

0.25 mmol) was heated with an oil bath to 190°C for 1 hr. The crude product was purified on SiO<sub>2</sub> (ethyl acetate/methanol 9:1, 1% NH<sub>3</sub> conc.) to yield 0.14 g (100%) of the ligand (**9**).

<sup>1</sup>H NMR (δ/ppm, CDCl<sub>3</sub>) 2.22 and 2.41 (6H, m), 7.00÷8.40 (19H, m), 9.30 (2H, m). FT-IR (KBr): 1719 cm<sup>-1</sup>. ESI m/z: 568 [M+H]<sup>+</sup>.

**3,4-bis(2-methylbenzo[b]thiophen-3-yl)-1H-pyrrole-2,5-dione (10)**. A solution of (**7**) (200 mg, 0.51 mmol), methanol (0.1 mL, 2.6 mmol) and DMF (0.2 mL) was treated with hexamethyldisilazane (1.1 mL, 5.2 mmol) at room temperature for 16 hr following a published procedure.<sup>iii</sup> 0.1N HCl<sub>aq</sub> was added and the mixture was extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulphate and the solvent was removed with a rotavapor. The crude product (**11**) (194 mg, 97%) was used without further purification.

<sup>1</sup>H NMR (δ/ppm, CDCl<sub>3</sub>) 2.03 (s, 3H), 2.3 (s, 3H), 7.00÷7.10 (m, 1H), 7.19÷7.40 (m, 4H), 7.50 (m, 1H), 7.65÷7.70 (m, 2H), 8.40 (s, 1H). ESI m/z: 390 [M+H]<sup>+</sup>.

**Methyl 1,10-phenanthroline-5-carboxylate (11)**. A solution 5-cyano-[1,10]-phenanthroline (1 g, 4.9 mmol), 2-methoxyethanol (5.5 mL) and 50% aqueous KOH (7.5 mL) was refluxed for 4 hr. The solution was concentrated and the residue was dissolved in hot water. The pH was adjusted to 2÷3 with conc. HCl and the precipitate was collected by filtration and dried (40°C). A mixture of the crude solid and thionylchloride (7 mL) was refluxed for 2 hr. The excess of thionylchloride was removed under vacuum and methanol was added with cooling (0°C). The solution was heated to reflux and stirred for 4 hr. The solvent was removed with a rotavapor to yield a white solid (**11**) (1 g, 90%).

<sup>1</sup>H NMR (δ/ppm, CDCl<sub>3</sub>) 4.07 (s, 3H), 7.70 (dd, J: 7.8, 4.4 Hz, 1H), 7.72 (dd, J: 8.6, 4.4 Hz, 1H), 8.34 (dd, J: 8.1 1.7 Hz, 1H), 8.61 (s, 1H), 9.23 (dd, J: 4.3, 1.7 Hz, 1H), 9.28 (dd, J: 4.4, 1.8 Hz, 1H), 9.42 (dd, J: 8.6, 1.3 Hz, 1H). IR (KBr) 1712 cm<sup>-1</sup>.

**5-(chloromethyl)-1,10-phenanthroline (12)**. The chloromethyl derivate was prepared from **11** following a published procedure.<sup>iv</sup>

$^1\text{H NMR}$  ( $\delta/\text{ppm}$ ,  $\text{CDCl}_3$ ) 5.11 (s, 2H), 7.70 (m, 1H), 7.76 (m, 1H), 7.90 (s, 1H), 8.25 (m, 1H), 8.60 (m, 1H), 9.25 (m, 2H). ESI  $m/z$  228  $[\text{M}]^+$ .

**1-((1,10-phenanthrolin-5-yl)methyl)-3,4-bis(2-methylbenzo[b]thiophen-3-yl)-1H-pyrrole-2,5-dione (13, phen-CH<sub>2</sub>-DAE)**. A solution of 5-chloromethyl-[1,10] phenanthroline **12** (45.6 mg, 0.2 mmol) in DMF (0.5 mL) was added to a mixture of **10** (100 mg, 0.26 mmol), Potassium *tert*-butoxide (28.8 mg, 0.26 mmol) and anhydrous THF (4 mL). The mixture was stirred and heated to 60°C for 4 hr, cooled to room temperature, diluted with water (5 mL) and extracted with  $\text{CH}_2\text{Cl}_2$  (2  $\times$  20 mL). The organic layers was collected, dried over anhydrous sulphate and concentrated under reduced pressure. The residue was purified with a flash chromatography (silica gel, ethyl acetate/methanol/conc.NH<sub>3</sub> 85%/14%/1%) to yield 0.135 g (90%) of the ligand (**12**).

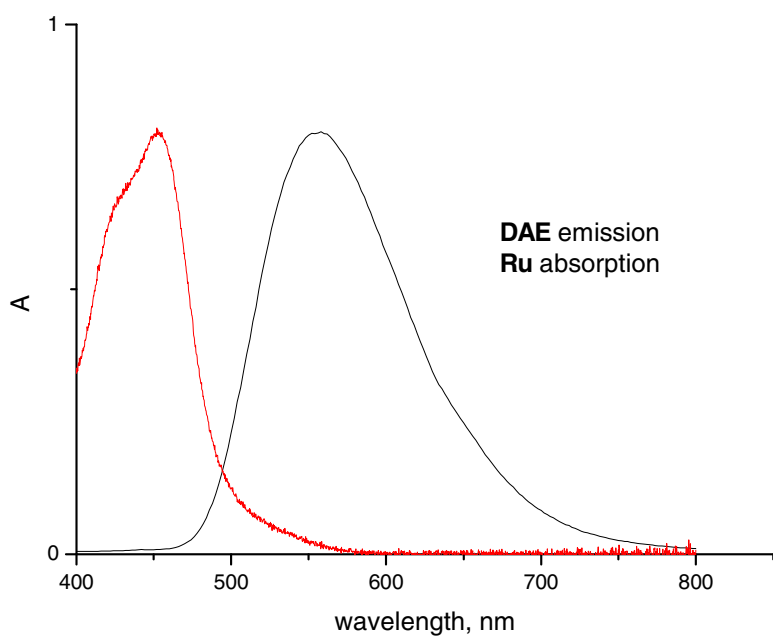
$^1\text{H NMR}$  ( $\delta/\text{ppm}$ ,  $\text{CDCl}_3$ ) 2.05 (s, 3H), 2.23 (s, 3H), 5.44 (s, 2H), 7.10 (m, 1H), 7.20÷7.30 (m, 4H), 7.38 (m, 1H) 7.61÷7.70 (m, 3H), 7.71÷7.79 (m, 1H), 8.15 (m, 1H) 8.36 (m, 1H), 8.98 (m, 1H), 9.30 (m, 2H). ESI  $m/z$ : 582  $[\text{M}+\text{H}]^+$ .

**[Ru(bpy)<sub>2</sub>phen-DAE](PF<sub>6</sub>)<sub>2</sub> (Ru-DAE)**. A solution of the ligand (**9**) (100 mg, 0.18 mmol),  $\text{Ru}(\text{bpy})_2\text{Cl}_2\cdot 2\text{H}_2\text{O}$  (113 mg, 0.19 mmol) in 10 mL of methanol was refluxed for 24 hr under an argon atmosphere. The solvent was removed under vacuum. Water was added and the excess of  $\text{Ru}(\text{bpy})_2\text{Cl}_2\cdot 2\text{H}_2\text{O}$  was removed with several extractions with chloroform. The aqueous layer was treated with an aqueous solution of 10%  $\text{NH}_4\text{PF}_6$ . The precipitate was collected by filtration, washed with water and dried to yield 0.2 g (90%) of an orange solid. All the procedures of the synthesis and purification of this complex were performed in the dark.

$^1\text{H NMR}$  ( $\delta/\text{ppm}$ ,  $\text{CD}_3\text{CN}$ ) 2.35÷2.40 (3H, m), 2.43÷2.47 (3H, m), 7.10÷8.85 (31H, m). ESI  $m/z$ : 497  $[\text{M} - 2\text{PF}_6]^{2+}$ .

**[Ru(bpy)<sub>2</sub>phen -CH<sub>2</sub>-DAE](PF<sub>6</sub>)<sub>2</sub> (Ru-CH<sub>2</sub>-DAE)**. This complex was prepared following the procedure for (**9**) using (**13**) as the ligand. The synthesis was performed in the dark.

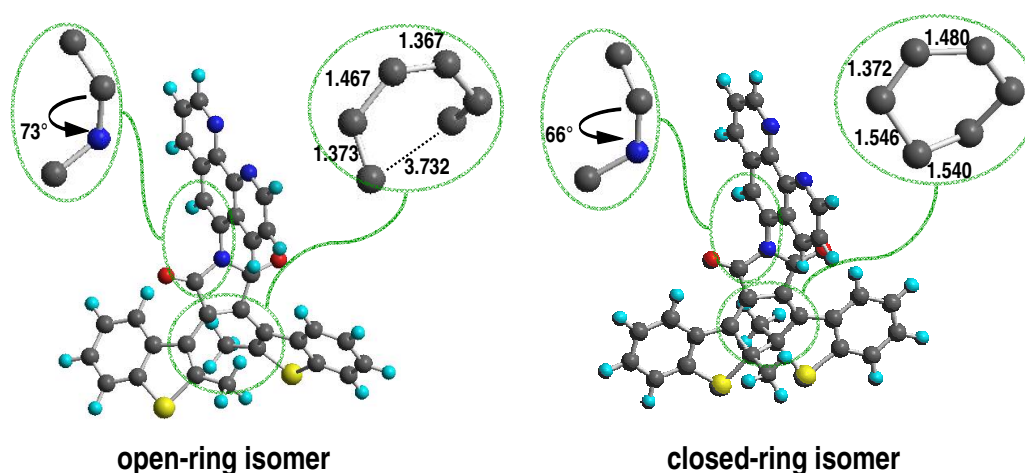
$^1\text{H}$  NMR ( $\delta/\text{ppm}$ ,  $\text{CD}_3\text{CN}$ ) 2.20÷2.25 (3H, m), 2.30÷2.35 (3H, m), 5.50 (2H, s), 7.05÷9.10 (31H, m) ESI m/z: 497  $[\text{M} - 2\text{PF}_6]^{2+}$ .



**Figure S1.** Spectral overlap between absorption of **Ru** (red line) and emission of **DAE** (black line) in  $\text{CH}_3\text{CN}$  (arbitrary units).

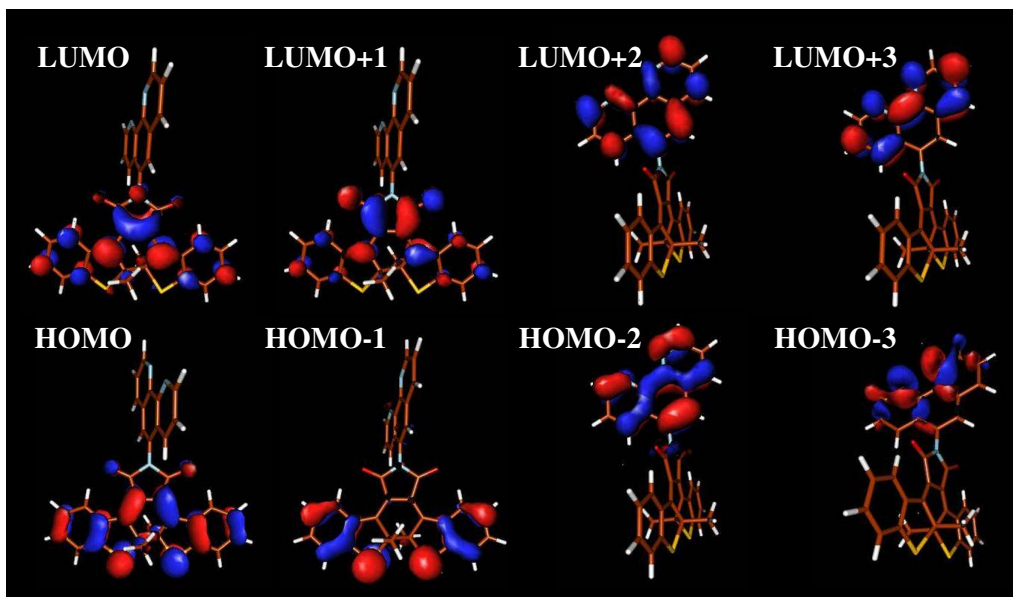
## DFT results on phen-DAE

**Phen-DAE.** The spectroscopic and photophysical results on **Ru-DAE** suggested a true supramolecular nature, with small electronic interaction between the two subunits of the dyad. The calculations on **phen-DAE** were meant to check the extent to which the diarylethene and phenanthroline moieties, though directly linked by a N-C bond, are effectively electronically decoupled. Geometry optimizations of the two ground state isomers, open- and closed-ring forms, have been carried out on **phen-DAE** at the B3LYP/6-31G level of accuracy. The two structures are presented in **Figure S2** along with the important geometrical parameters. Both the open- and closed-ring structures show  $C_2$  symmetry of the diarylethene fragment, a feature common to all the systems investigated here (*vide infra*). However, the phenanthroline planar fragment and the central 5-membered ring of the diarylethene fragment are strongly twisted around the connecting C-N bond. The dihedral angles are  $73^\circ$  and  $66^\circ$  for the open- and closed-ring isomer equilibrium geometries, respectively. A relaxed scan about the C-N bond describes a flat PES within the range  $73^\circ$ - $66^\circ$ , for both isomers.



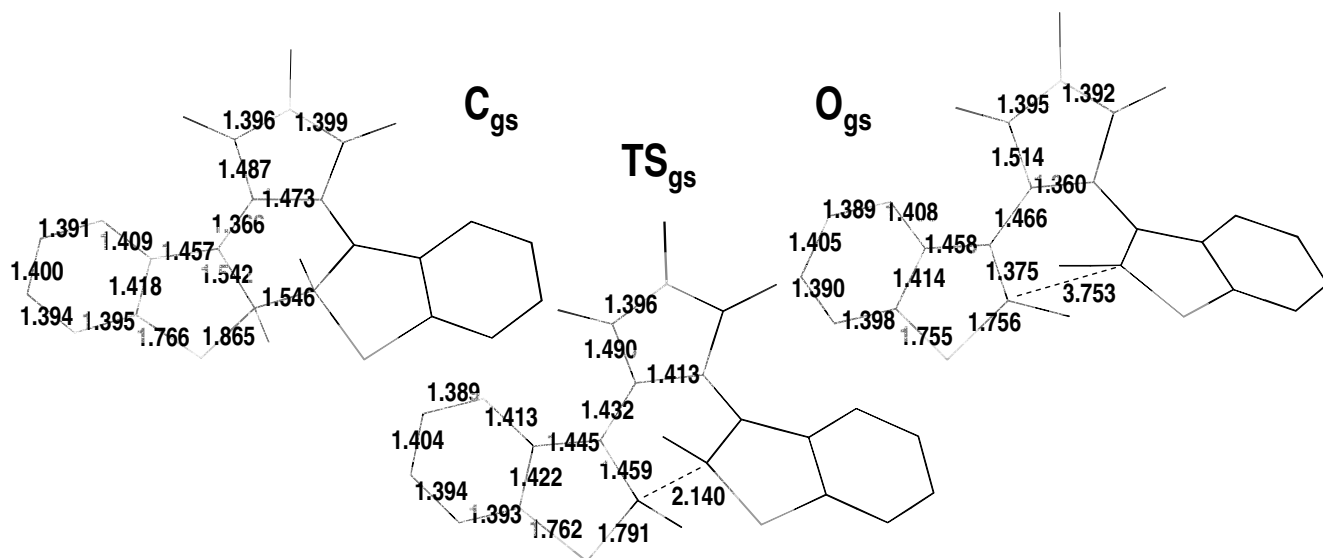
**Figure S2.** Optimized structures on the  $S_0$  PES at the B3LYP/6-31G level, for **phen-DAE**. Open-ring isomer ( $E_h = -2418.8959$ ). Closed-ring isomer ( $E_h = -2418.9034$ ). Distances in Å.

The low torsional barrier is explained by looking at the MOs plot provided in **Figure S3**. Neglecting the contributions due to dipole-dipole interactions and van der Waals interactions between the two moieties, the contribution from conjugation is missing (MOs are localised either on phenanthroline or on diarylethene), whereas the steric and bonding/antibonding interactions become important only at higher torsional angles.

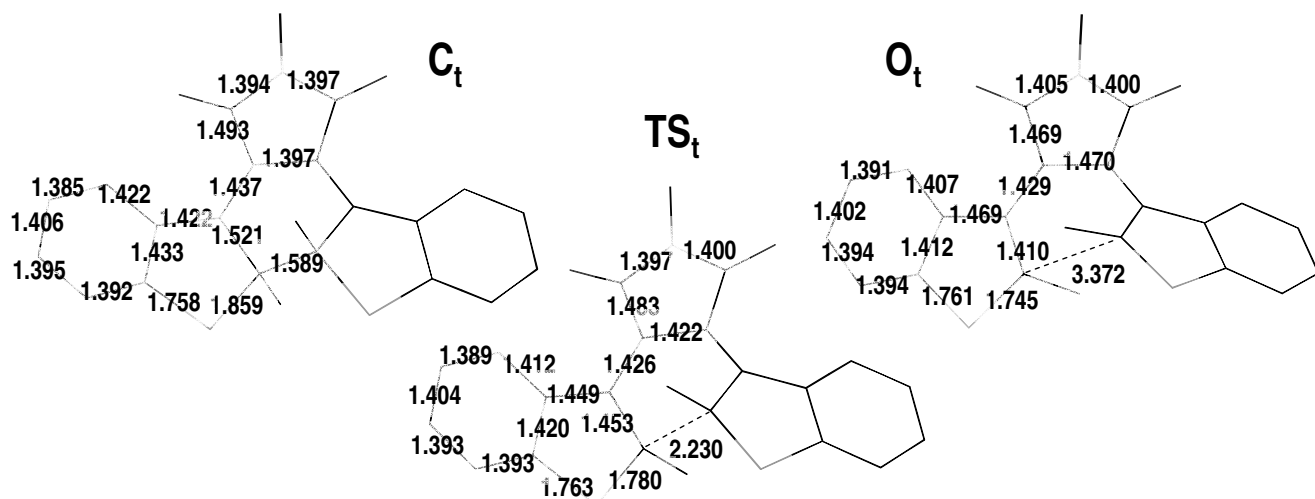


**Figure S3.** Frontier molecular orbitals' contour plot of the closed-ring isomer  $S_0$  equilibrium geometry at the B3LYP/6-31G\* level, for **phen-DAE**.

## DFT results on DAE



**Figure S4.** Optimized structures on  $S_0$  PES at the B3LYP/6-31G\* level, for **DAE**. Closed-ring isomer ( $C_{gs}$ ), transition state ( $TS_{gs}$ ) and open-ring isomer ( $O_{gs}$ ). Distances in Å.



**Figure S5.** Optimized structures on  $T_1$  PES at the UB3LYP/6-31G\* level, for **DAE**. Closed-ring isomer ( $C_t$ ), transition state ( $TS_t$ ) and open-ring isomer ( $O_t$ ). Distances in Å.

**Table A.** UB3LYP/6-31G energies at the relative optimized geometries for **DAE**.

geometry	$q$ /Å	$S_0$ /h; S <sup>2</sup>	$\Delta E(S_0)$ /kcal mol <sup>-1</sup>	$T_1$ /h; S <sup>2</sup>	$\Delta E(T_1)$ /kcal mol <sup>-1</sup>
<b>O<sub>gs</sub></b>	3.75	-1887.9536; 0.000	0.00	-1888,2233; 2.001	51.90
<b>O<sub>t</sub></b>	3.32	-1887.9322; 0.000	13.43	-1887.8923; 2.000	38.47
<b>C<sub>t</sub></b>	1.58	-1887.9431; 0.000	6.59	-1887.9083; 2.001	28.43
<b>C<sub>gs</sub></b>	1.54	-1887.9616; 0.000	-5.02	-1887.8919; 2.000	38.72

$\Delta E(S_0)$  and  $\Delta E(T_1)$  are calculated with the open-ring  $S_0$  minimum energy as reference. The wavefunction spin-contamination is reported along with the absolute energy values.

**CASSCF, CASPT2 and DFT results on mod-DAE**

**Table B.** CASSCF(10,10)/6-31G\* energies and CASPT2(10,10)/6-31G\* corrections (in brackets), at the relative optimized geometries, for **mod-DAE**.

geometry	$q$ /Å	$S_0$ /h	$\Delta E(S_0)$ /kcal mol <sup>-1</sup>	$T_1$ /h	$\Delta E(T_1)$ /kcal mol <sup>-1</sup>	$\Delta E(T_1-S_0)$ /kcal mol <sup>-1</sup>
$O_t$	3.96	-1178.3632	45.2	-1178.3636 (-1179.7862)	44.9 (42.0)	-0.2
$O_{gs}$	3.42	-1178.4352 (-1179.8531)	0.0 (0.0)	-1178.3081	79.8	79.8
$TS_t$	2.23	-1178.3564	49.4	-1178.3284 (-1179.7789)	67.0 (46.6)	17.6
$TS_{gs}$	2.04	-1178.3494 (-1179,7908)	53.8 (39.1)	-1178.3342	63.4	9.5
$C_t$	1.57	-1178.3975	23.7	-1178.3715 (-1179.8113)	40.0 (26.2)	16.3
$C_{gs}$	1.55	-1178.4299 (-1179.8528)	3.3 (0.2)	-1178.3387	60.6	57.2

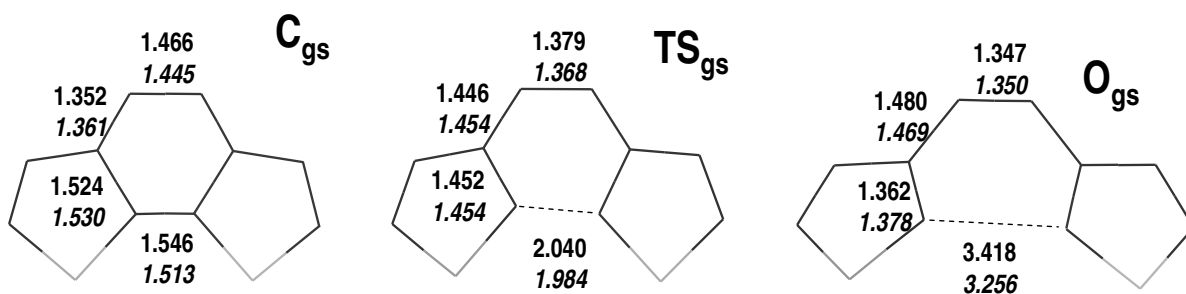
$\Delta E(S_0)$  and  $\Delta E(T_1)$  are calculated with the open-ring  $S_0$  minimum energy as reference.

**Table C.** UB3LYP/6-31G\* energies at the relative optimized geometries for **mod-DAE**.

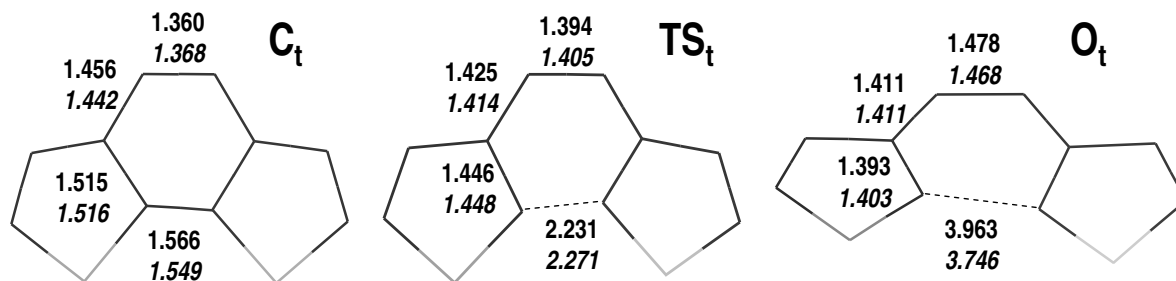
geometry	$q$ /Å	$S_0; S^2$ /h	$\Delta E(S_0)$ /kcal mol <sup>-1</sup>	$T_1; S^2$ /h	$\Delta E(T_1)$ /kcal mol <sup>-1</sup>	$\Delta E(T_1-S_0)$ /kcal mol <sup>-1</sup>
<b>O<sub>t</sub></b>	3.75	-1182.1491; 0.363	39.2	-1182.1464; 2.000 (-1182.0022)	40.9	1.7
<b>O<sub>gs</sub></b>	3.26	-1182.2116; 0.000 (-1182.0633)	0.0	-1182.1115; 2.000	62.8	62.8
<b>TS<sub>t</sub></b>	2.27	-1182.1431; 0.260	43.0	-1182.1307; 2.001 (-1181,9854)	50.7	7.8
<b>TS<sub>gs</sub></b>	1.90	-1182.1403; 0.432 (-1181.9954)	44.7	-1182.1351; 2.004	48.0	3.3
<b>C<sub>t</sub></b>	1.55	-1182.1843; 0.059	17.1	-1182.1646; 2.000 (-1182,0173)	29.5	12.3
<b>C<sub>gs</sub></b>	1.51	-1182.2062; 0.000 (-1182.0563)	3.3	-1182.1430; 2.000	43.0	39.7

$\Delta E(S_0)$  and  $\Delta E(T_1)$  are calculated with the open-ring  $S_0$  minimum energy as reference. In brackets are the zero-point-energy-corrected UB3LYP/6-31G\* energies. The wavefunction spin-contamination is reported along with the absolute energy values.

The equilibrium structures are detailed in **Figures S6-7**. The CASSCF and CASPT2 results on **mod-DAE** are benchmarked against the DFT calculations. The DFT results on **mod-DAE** are also compared with those of **DAE** (discussed in the previous section). This approach facilitates a discussion which is both focused on the differences between the two compounds (**DAE** and **mod-DAE**) and the two levels of theory applied (CASSCF//CASPT2 and DFT).



**Figure S6.** Optimized structures on S<sub>0</sub> PES at the CASSCF(10,10)/6-31G\* (regular) and UB3LYP/6-31G\* (italic) levels of theory, for **mod-DAE**. Closed-ring isomer (C<sub>gs</sub>), transition state (TS<sub>gs</sub>) and open-ring isomer (O<sub>gs</sub>). Distances in Å.



**Figure S7.** Optimized structures on T<sub>1</sub> PES at the CASSCF(10,10)/6-31G\* (regular) and UB3LYP/6-31G\* (italic) levels of theory, for **mod-DAE**. Closed-ring isomer (C<sub>t</sub>), transition state (TS<sub>t</sub>) and open-ring isomer (O<sub>t</sub>). Distances in Å.

# GEOMETRIES

## Phen-DAE (B3LYP/6-31G)

### Open-ring isomer

C	-0.999269	0.683754	0.207527	-0.063579
C	-0.983832	-0.550927	-0.378552	-0.057447
C	-2.130697	1.480874	0.693080	0.068599
C	-2.348921	2.882160	0.325492	0.160376
C	-3.079586	0.979400	1.549973	-0.144424
C	-3.506257	3.435927	0.918362	-0.161025
S	-4.343215	2.220234	1.978612	0.208535
C	-1.595767	3.695807	-0.544132	-0.162239
C	-1.996775	5.007775	-0.788357	-0.144572
C	-3.150454	5.535370	-0.180307	-0.120565
C	-3.917366	4.747888	0.680935	-0.174968
C	-3.192953	-0.374788	-2.171975	-0.513576
C	-2.096570	-1.389619	-0.836188	0.069019
C	-2.248304	-2.800510	-0.470998	0.160066
C	-3.090212	-0.921765	-1.660975	-0.144791
C	-3.401914	-3.395780	-1.030076	-0.161094
S	-4.317963	-2.208549	-2.056517	0.208825
C	-1.435710	-3.589986	0.366791	-0.164747
C	-1.776867	-4.918163	0.614148	-0.144717
C	-2.929096	-5.486394	0.041047	-0.120372
C	-3.753921	-4.724088	-0.788725	-0.174839
C	-3.274506	0.429004	-2.273250	-0.513911
C	0.425894	1.138096	0.394120	0.585804
C	0.451830	-0.950423	-0.602690	0.578782
O	0.832343	2.192318	0.892664	-0.472067
O	0.885364	-1.977222	-1.135283	-0.472917
N	1.248370	0.101780	-0.101428	-0.657647
C	2.680474	0.135978	-0.136813	0.241752
H	-0.695423	3.312218	-1.007787	0.132745
H	-1.408440	5.631457	-1.453117	0.134754
H	-3.447840	6.559509	-0.379513	0.136032
H	-4.809620	5.145678	1.151554	0.144836
H	-0.534156	-3.176193	0.801324	0.134034
H	-1.142066	-5.522868	1.253161	0.135334
H	-3.179702	-6.522584	0.242201	0.136285
H	-4.645028	-5.153492	-1.232989	0.144869
H	-3.499787	-0.303514	3.220766	0.175191
H	-3.931275	-0.997008	1.650497	0.194605
H	-2.236301	-0.902418	2.131690	0.171155
H	-3.615100	0.349078	-3.310932	0.175011
H	-4.016196	1.022649	-1.723995	0.194561
H	-2.336847	0.991011	-2.264700	0.172736
C	3.432554	-0.666487	0.798372	0.175664
C	4.859836	-0.637978	0.755900	0.189355
C	5.530918	0.214213	-0.210760	0.236598
C	4.743345	1.005709	-1.097370	0.151912
C	3.313513	0.939609	-1.040491	-0.204308
C	2.816920	-1.484034	1.775623	-0.141838
C	3.601025	-2.229766	2.637176	-0.147799
C	5.004274	-2.152633	2.511811	0.046472
N	5.616870	-1.383997	1.609183	-0.477656
C	5.416335	1.835823	-2.027044	-0.154185
C	6.799268	1.853071	-2.047839	-0.147604
C	7.497259	1.033771	-1.133091	0.045260
N	6.893491	0.240954	-0.244019	-0.479854
H	2.731379	1.538752	-1.732651	0.143879
H	1.736196	-1.512042	1.846652	0.141184
H	3.154891	-2.862343	3.396218	0.141029
H	5.649240	-2.729782	3.167161	0.149088
H	4.837496	2.448090	-2.711856	0.146225
H	7.344971	2.477139	-2.746503	0.142809
H	8.582887	1.022426	-1.123950	0.149439

### Closed-ring isomer

C	-0.837273	0.775561	-0.052503	-0.005333
C	-0.831601	-0.700019	-0.164749	-0.001550
C	-1.989500	1.495877	0.133236	-0.006149
C	-2.270105	2.927453	0.207168	0.124988
C	-3.245050	0.633815	0.396689	-0.192443
C	-3.655819	3.236195	0.196282	-0.125927
S	-4.754729	1.786889	0.074200	0.144346
C	-1.353712	4.002722	0.265859	-0.164873
C	-1.819398	5.316432	0.324466	-0.151921
C	-3.194641	5.591549	0.319858	-0.107441
C	-4.123159	4.546905	0.255494	-0.180802
C	-3.266452	0.269448	1.903370	-0.430319
C	-1.981598	-1.431746	-0.318163	-0.006944
C	-2.249989	-2.865980	-0.379532	0.124702
C	-3.252153	-0.582268	-0.547463	-0.192753
C	-3.631771	-3.188304	-0.328359	-0.125887
S	-4.741317	-1.749309	-0.183188	0.144392
C	-1.324632	-3.932374	-0.458490	-0.165470
C	-1.778458	-5.250960	-0.496263	-0.152093
C	-3.150228	-5.539620	-0.451425	-0.107411
C	-4.087207	-4.503946	-0.367205	-0.180833
C	-3.317786	-0.218687	-2.052978	-0.430667
C	0.570854	1.222294	-0.090788	0.591072
C	0.581052	-1.131700	-0.169569	0.583534
O	1.064767	2.363322	-0.078881	-0.509169
O	1.088935	-2.265794	-0.230984	-0.511193
N	1.360464	0.047104	-0.121221	-0.666449
C	2.793617	0.056303	-0.162330	0.251032
H	-0.292836	3.795225	0.256805	0.214220
H	-1.105264	6.131277	0.373523	0.142965
H	-3.545538	6.617557	0.365138	0.143159
H	-5.187662	4.752205	0.250473	0.149127
H	-0.266170	-3.713648	-0.483388	0.215354
H	-1.057788	-6.058918	-0.560934	0.143449
H	-3.491878	-6.569322	-0.480953	0.143284
H	-5.148992	-4.719947	-0.331090	0.149125
H	-4.181553	-0.267113	2.157871	0.189346
H	-2.407110	-0.360294	2.155796	0.163660
H	-3.216280	1.182926	2.501363	0.168645
H	-4.243339	0.311422	-2.281991	0.189070
H	-2.470093	0.416650	-2.329425	0.165370
H	-3.277901	-1.132195	-2.651685	0.168648
C	3.544734	-0.407906	0.980259	0.175340
C	4.972220	-0.393181	0.930168	0.188156
C	5.643725	0.106207	-0.257547	0.235734
C	4.856278	0.575881	-1.349119	0.150900
C	3.426894	0.533639	-1.273404	-0.203038
C	2.930736	-0.871139	2.168452	-0.136688
C	3.716675	-1.300675	3.222417	-0.149065
C	5.119618	-1.265908	3.078498	0.045753
N	5.730798	-0.826078	1.976914	-0.478763
C	5.528970	1.068350	-2.494331	-0.154759
C	6.911893	1.076919	-2.520458	-0.148089
C	7.609937	0.589088	-1.393554	0.044789
N	7.006502	0.119915	-0.298413	-0.480456
H	2.845087	0.890746	-2.116103	0.147819
H	1.850849	-0.884344	2.245881	0.144186
H	3.270895	-1.659755	4.143120	0.141159
H	5.765579	-1.602513	3.883603	0.147369
H	4.949598	1.433331	-3.336962	0.146455
H	7.457473	1.447226	-3.381099	0.141534
H	8.695648	0.580051	-1.382085	0.147965

## DAE (UB3LYP/6-31G\*)

O<sub>gs</sub>

C	0.651911	1.043731	-0.196038
C	-0.651403	1.044869	0.194825
C	1.539209	-0.070410	-0.543385
C	2.878775	-0.243966	0.004092
C	1.199540	-1.056161	-1.439503
C	3.514095	-1.401247	-0.501667
S	2.483612	-2.234901	-1.652121
C	3.566315	0.533142	0.954259
C	4.838919	0.156360	1.362064
C	5.453377	-0.995341	0.841839
C	4.794845	-1.784561	-0.094296
C	-0.059282	-1.222997	-2.235180
C	-1.540353	-0.067959	0.543383
C	-2.878719	-0.242805	-0.006359
C	-1.202769	-1.051004	1.443101
C	-3.515642	-1.398118	0.501892
S	-2.487657	-2.228825	1.656726
C	-3.563812	0.531503	-0.960566
C	-4.835783	0.154069	-1.369771
C	-5.452004	-0.995471	-0.846838
C	-4.795809	-1.781987	0.093223
C	0.054706	-1.215924	2.241316
C	1.099541	2.483777	-0.328319
C	-1.098321	2.484662	0.328350
O	2.185686	2.909994	-0.667043
O	-2.186114	2.905461	0.668174
N	0.002615	3.275651	0.000345
C	0.009749	4.727027	-0.000669
H	3.112788	1.433492	1.353428
H	5.368174	0.763470	2.091051
H	6.450461	-1.272719	1.172022
H	5.262532	-2.677830	-0.498155
H	-3.108665	1.429955	-1.362285
H	-5.363122	0.758889	-2.102044
H	-6.448583	-1.273375	-1.178099
H	-5.264839	-2.673653	0.499066
H	0.158527	-1.578667	-3.248005
H	-0.737534	-1.946844	-1.766849
H	-0.597164	-0.274896	-2.313945
H	-0.164938	-1.566944	3.255373
H	0.732769	-1.942598	1.777081
H	0.593544	-0.268092	2.316729
H	-0.983627	5.058531	0.305427
H	0.759792	5.106201	0.699551
H	0.238463	5.108949	-1.000030

C<sub>gs</sub>

C	-1.263257	0.326014	-0.649261
C	-1.252396	-0.363871	0.652471
C	-0.120513	0.581533	-1.352520
C	0.147499	1.290856	-2.597181
C	1.158142	-0.053262	-0.770797
C	1.532897	1.487913	-2.826022
S	2.587119	0.849492	-1.561044
C	-0.766368	1.799586	-3.541053
C	-0.301073	2.467592	-4.669223
C	1.071534	2.645305	-4.878721
C	1.997351	2.154547	-3.959009
C	1.208149	-1.523948	-1.259438
C	-0.101115	-0.585397	1.354161
C	0.191823	-1.285335	2.598931
C	1.157076	0.087468	0.769333
C	1.583314	-1.440335	2.823858
S	2.614481	-0.771234	1.556283
C	-0.702712	-1.820360	3.546873
C	-0.213812	-2.473305	4.673822
C	1.164151	-2.609954	4.878696
C	2.071477	-2.092041	3.955581
C	1.163843	1.559110	1.257777
C	-2.688106	0.549542	-1.007614
C	-2.669261	-0.632205	1.014293
O	-3.205532	1.101781	-1.967536
O	-3.158517	-1.204170	1.977052
N	-3.441393	-0.051551	0.002366

C	-4.892669	-0.067805	-0.010499
H	-1.827043	1.666949	-3.371966
H	-1.013670	2.852685	-5.392699
H	1.423618	3.169192	-5.763380
H	3.062792	2.290420	-4.118978
H	-1.767282	-1.719632	3.381958
H	-0.912166	-2.878798	5.400034
H	1.534799	-3.122537	5.762389
H	3.141088	-2.195544	4.111881
H	2.135970	-2.006630	-0.947222
H	0.364402	-2.092470	-0.856659
H	1.151934	-1.545959	-2.350927
H	2.075918	2.069216	0.942770
H	0.302254	2.101933	0.857352
H	1.110039	1.579691	2.349408
H	-5.222664	-0.606955	0.877846
H	-5.282491	0.954181	0.001667
H	-5.256556	-0.567479	-0.912956

TS<sub>gs</sub>

C	-0.701535	1.284801	0.106378
C	0.663813	1.246942	-0.251662
C	-1.469610	0.124392	0.441971
C	-2.858717	-0.144589	0.148583
C	-0.741389	-1.057347	0.891234
C	-3.194257	-1.515640	0.319028
S	-1.836952	-2.473054	0.906816
C	-3.863252	0.731275	-0.321397
C	-5.133505	0.241705	-0.594714
C	-5.437284	-1.118454	-0.426623
C	-4.463966	-2.008147	0.025990
C	0.180493	-1.011311	2.096476
C	1.407392	0.036161	-0.430242
C	2.788551	-0.222843	-0.093868
C	0.654411	-1.177000	-0.726905
C	3.093619	-1.611546	-0.083538
S	1.718136	-2.606408	-0.555307
C	3.810145	0.683497	0.269442
C	5.067026	0.205044	0.614946
C	5.340443	-1.171769	0.625581
C	4.349652	-2.090413	0.281929
C	-0.267504	-1.266447	-1.929486
C	-1.125861	2.712969	0.118007
C	1.120023	2.650302	-0.455000
O	-2.207226	3.212358	0.389292
O	2.214100	3.076870	-0.791067
N	0.003699	3.460030	-0.220645
C	0.009754	4.907310	-0.314763
H	-3.642717	1.785548	-0.429852
H	-5.903336	0.924730	-0.942374
H	-6.436544	-1.483334	-0.647181
H	-4.691774	-3.062369	0.153973
H	3.613280	1.747514	0.241435
H	5.850117	0.909870	0.879572
H	6.329531	-1.527190	0.900653
H	4.553582	-3.157160	0.292664
H	-0.417602	-0.963670	3.013549
H	0.807880	-1.906820	2.147807
H	0.829260	-0.134600	2.069747
H	0.330497	-1.351344	-2.843935
H	-0.915554	-2.146413	-1.865823
H	-0.895544	-0.378723	-2.017303
H	-0.732229	5.244004	-1.044647
H	-0.226584	5.356294	0.654854
H	1.008690	5.210079	-0.631488

O<sub>t</sub>

C	0.731812	1.109528	-0.068974
C	-0.732122	1.110903	0.068772
C	1.556353	0.000253	-0.430927
C	2.936091	-0.205181	0.029121
C	1.127950	-1.065835	-1.248873
C	3.470795	-1.440619	-0.396330
S	2.329076	-2.322244	-1.405918
C	3.722923	0.597324	0.875515
C	4.993623	0.169870	1.247754
C	5.502402	-1.059104	0.805881

C	4.738195	-1.881385	-0.019449
C	-0.092766	-1.187604	-2.114047
C	-1.558292	0.002110	0.430984
C	-2.936579	-0.205180	-0.032441
C	-1.131569	-1.061030	1.252819
C	-3.472338	-1.439048	0.396281
S	-2.333224	-2.316664	1.412097
C	-3.720648	0.593117	-0.885359
C	-4.989871	0.163711	-1.260141
C	-5.500052	-1.063317	-0.814298
C	-4.738472	-1.881729	0.017145
C	0.088153	-1.180477	2.119772
C	1.172200	2.511295	-0.045531
C	-1.173972	2.512265	0.049155
O	2.293373	3.011177	-0.122538
O	-2.298847	3.002829	0.127510
N	0.001570	3.278962	0.002903
C	0.014887	4.727381	0.001162
H	3.352855	1.561191	1.198067
H	5.599738	0.802717	1.889551
H	6.496365	-1.376852	1.108115
H	5.118508	-2.840531	-0.358513
H	-3.349538	1.555200	-1.211917
H	-5.593768	0.793346	-0.1907167
H	-6.492922	-1.382590	-1.118500
H	-5.119609	-2.839548	0.359023
H	0.199939	-1.416255	-3.145978
H	-0.757622	-1.992728	-1.777961
H	-0.663625	-0.259682	-2.124727
H	-0.205731	-1.404933	3.152275
H	0.752557	-1.987465	1.787293
H	0.659852	-0.253038	2.127306
H	-1.020995	5.064685	0.052050
H	0.578007	5.103398	0.861038
H	0.491126	5.102001	-0.910488

**C<sub>i</sub>**

C	-1.299973	0.190207	-0.664792
C	-1.293463	-0.226999	0.668469
C	-0.092368	0.413816	-1.409272
C	0.166275	1.206169	-2.561432
C	1.150565	-0.183894	-0.766865
C	1.564424	1.371938	-2.825407
S	2.601827	0.529507	-1.683153
C	-0.750296	1.862231	-3.427911
C	-0.280329	2.624683	-4.484267
C	1.098358	2.771611	-4.719153
C	2.026044	2.144677	-3.886612
C	1.187747	-1.716495	-0.959054
C	-0.078188	-0.416073	1.412050
C	0.207212	-1.207775	2.557910
C	1.143798	0.224347	0.770742
C	1.610231	-1.326943	2.821950
S	2.618108	-0.440402	1.686671
C	-0.686118	-1.902409	3.418759
C	-0.190384	-2.655321	4.470145
C	1.192405	-2.755233	4.705590
C	2.098013	-2.090379	3.878066
C	1.129909	1.757288	0.962678
C	-2.724336	0.288556	-1.104460
C	-2.712407	-0.363544	1.113300
O	-3.201044	0.571522	-2.192009
O	-3.170356	-0.659857	2.205157
N	-3.500864	-0.047253	0.003776
C	-4.950985	-0.067380	-0.004979
H	-1.812376	1.734761	-3.264085
H	-0.991391	3.114453	-5.143578
H	1.446722	3.374760	-5.552773
H	3.091964	2.257951	-4.061389
H	-1.751861	-1.811716	3.255169
H	-0.884274	-3.174724	5.125073
H	1.561138	-3.351593	5.535311
H	3.167167	-2.167591	4.052769
H	2.110644	-2.135649	-0.549297
H	0.337053	-2.187108	-0.457648
H	1.138477	-1.955864	-2.024634
H	2.039376	2.206818	0.555059

H	0.265455	2.199512	0.458953
H	1.070192	1.994944	2.028097
H	-5.279222	-0.364339	0.991946
H	-5.346612	0.923620	-0.246912
H	-5.319353	-0.781392	-0.747696

**TS<sub>i</sub>**

C	-0.667689	1.275956	0.154707
C	0.711424	1.249209	-0.189398
C	-1.435494	0.110151	0.445700
C	-2.829781	-0.141006	0.144721
C	-0.731418	-1.089864	0.866992
C	-3.171842	-1.514172	0.262300
S	-1.818421	-2.498461	0.817502
C	-3.827242	0.757616	-0.293958
C	-5.099660	0.284960	-0.587944
C	-5.410026	-1.078845	-0.472220
C	-4.442584	-1.990500	-0.051681
C	0.234004	-1.106635	2.033449
C	1.441193	0.051285	-0.448864
C	2.824798	-0.239883	-0.135314
C	0.697858	-1.133379	-0.843526
C	3.120550	-1.626138	-0.220319
S	1.736767	-2.576056	-0.759863
C	3.850020	0.633740	0.289675
C	5.104052	0.124790	0.601518
C	5.368436	-1.250988	0.517581
C	4.372634	-2.138330	0.111625
C	-0.268410	-1.145804	-2.009286
C	-1.086578	2.696778	0.221557
C	1.177943	2.651840	-0.300248
O	-2.172279	3.195670	0.489987
O	2.282136	3.097839	-0.585154
N	0.056404	3.452366	-0.051462
C	0.070115	4.901693	-0.072301
H	-3.598177	1.813776	-0.360235
H	-5.865569	0.984293	-0.910781
H	-6.410452	-1.430246	-0.708959
H	-4.675776	-3.047682	0.035312
H	3.656752	1.698127	0.332761
H	5.891555	0.804658	0.913810
H	6.355041	-1.630780	0.768055
H	4.569894	-3.204560	0.049736
H	-0.330186	-1.128209	2.973397
H	0.875031	-1.994062	2.006079
H	0.867398	-0.219107	2.040522
H	0.294160	-1.207561	-2.948420
H	-0.937894	-2.011106	-1.961299
H	-0.872630	-0.238580	-2.037108
H	1.078204	5.214975	-0.347205
H	-0.651637	5.278819	-0.802943
H	-0.190480	5.303238	0.912011

**mod-DAE (CAS-SCF(10,10)/6-31G\*)****O<sub>gs</sub>**

C	-0.09627	.673316	1.987797
C	.019239	1.606238	.839120
C	.807765	1.506272	-.266476
C	-.780929	2.817522	.809531
C	-.581243	3.560884	-.305940
S	.593715	2.836497	-1.366305
H	-.037302	1.155113	2.951549
H	1.503756	.726896	-.496880
H	-1.466861	3.089195	1.590251
H	-1.051954	4.486076	-.568231
C	.009627	-.673316	1.987797
C	-.019239	-1.606238	.839120
C	-.807765	-1.506272	-.266476
C	.780929	-2.817522	.809531
C	.581243	-3.560884	-.305940
S	-.593715	-2.836497	-1.366305
H	.037302	-1.155113	2.951549
H	-1.503756	-.726896	-.496880
H	1.466861	-3.089195	1.590251
H	1.051954	-4.486076	-.568231

**C<sub>gs</sub>**

C	-1.697712	-.389173	-1.597802
C	-1.734381	-.358120	-.247260
C	-.436142	-.383515	.550666
C	-2.898472	-.286619	.629623
C	-2.595036	-.011684	1.910519
S	-.865805	.197147	2.237056
H	-2.607018	-.422167	-2.171483
H	-.082481	-1.406466	.629133
H	-3.903514	-.405357	.269889
H	-3.292003	.106990	2.716163
C	-.410079	-.372257	-2.297806
C	.713453	-.010686	-1.639615
C	.631048	.453924	-.190442
C	2.089754	-.005527	-2.124290
C	3.004930	.159756	-1.152956
S	2.335093	.333627	.478475
H	-.372466	-.654157	-3.335184
H	.334200	1.497399	-.163905
H	2.341311	-.158982	-3.157145
I	4.069178	.173761	-1.279791

**TS<sub>gs</sub>**

C	-.023480	-.023963	-.060082
C	.026473	-.035779	1.367850
C	1.288395	-.058152	2.079312
C	-1.107184	.158431	2.237047
C	-.804465	.290965	3.555011
S	.979480	.141610	3.881173
H	-.950243	-.275014	-.541868
H	2.058792	-.759474	1.837220
H	-2.108511	.235588	1.861523
H	-1.470379	.496227	4.362933
C	1.087749	.304116	-.843675
C	2.263555	.897653	-.289780
C	2.252720	1.513659	1.021534
C	3.586729	.793470	-.852594
C	4.584527	1.278168	-.067928
S	3.967705	1.981241	1.492957
H	1.063885	.104046	-1.898871
H	1.506356	2.226359	1.302545
H	3.769204	.327807	-1.801006
H	5.634750	1.255406	-.254553

**O<sub>t</sub>**

C	-.407222	.622686	1.625613
C	-.118246	1.727825	.796855
C	.890067	1.790771	-.161597
C	-.863235	2.985031	.836106
C	-.414075	3.903611	-.045575
S	.939586	3.320526	-.990396
H	-1.218002	.718259	2.328585
H	1.582862	1.015545	-.413467

H	-1.685401	3.155105	1.505879
H	-.791257	4.893516	-.202695
C	.366851	-.635555	1.631747
C	.107615	-1.731238	.780936
C	-.867162	-1.784110	-.212196
C	.852998	-2.987834	.830805
C	.436285	-3.896266	-.076924
S	-.885769	-3.304085	-1.060076
H	1.152892	-.739060	2.361206
H	-1.552247	-1.006860	-.478507
H	1.652445	-3.164497	1.525896
H	.821016	-4.883371	-.233363

**C<sub>t</sub>**

C	-1.6662893804	-0.493086542	-1.6679368694
C	-1.7120126777	-0.4272373542	-0.214081168
C	-0.400210271	-0.4467077316	0.5421951616
C	-2.8278968169	-0.2254014008	0.591375222
C	-2.5373039559	-0.0075872863	1.9318971123
S	-0.8095499924	-0.0232072701	2.2780446769
H	-2.5740813709	-0.7045984586	-2.2044502896
H	0.0356924226	-1.4379228088	0.5286873272
H	-3.8323750998	-0.2019388836	0.20942087
H	-3.238735115	0.1953946181	2.7143046535
C	-0.5012456252	-0.2868418681	-2.3386985776
C	0.7171321876	0.0700982185	-1.6257133944
C	0.5939190491	0.5209308781	-0.185279323
C	2.0291021979	-0.0660674304	-2.0672139031
C	2.9907314544	0.1681285165	-1.0928711546
S	2.3017536482	0.5673732542	0.4790578836
H	-0.462501722	-0.3903578663	-3.4084884516
H	0.1810287419	1.5204656889	-0.1298089883
H	2.2848759884	-0.3642084164	-3.0677674239
H	4.0518256194	0.0906658749	-1.2088287702

**TS<sub>t</sub>**

C	-1.6460940048	-0.4476917225	-1.5860374976
C	-1.7277543272	-0.4771417321	-0.1637912586
C	-0.5699189189	-0.7119384275	0.6703658484
C	-2.8837629113	-0.1308398084	0.6146657491
C	-2.6522475748	-0.0937062273	1.9543550347
S	-1.0009175002	-0.5266032935	2.376990555
H	-2.5560836057	-0.5545324772	-2.1504633724
H	0.1329625461	-1.4880674615	0.4440776677
H	-3.8296802582	0.1234805834	0.1735188195
H	-3.3434029035	0.1942591739	2.7199454008
C	-0.4384880364	-0.3056222782	-2.2671370326
C	0.7587837834	0.1273593233	-1.6272957544
C	0.7510035612	0.7782598888	-0.335860296
C	2.0942641093	-0.1545218005	-2.0737432533
C	3.0595857919	0.240819413	-1.2010457035
S	2.4093424902	1.0365389037	0.2261623125
H	-0.4044391002	-0.5161058354	-3.3219409185
H	0.0499463739	1.5551359058	-0.1064961578
H	2.3058989894	-0.6748786247	-2.9894339898
H	4.114860778	0.0836902287	-1.2929915598

**mod-DAE (UB3LYP/6-31G\*)****O<sub>gs</sub>**

C	-0.062523	0.672225	1.866979
C	-0.093576	1.654766	0.776330
C	0.489083	1.552541	-0.468155
C	-0.705144	2.947859	0.954257
C	-0.590059	3.763779	-0.131909
S	0.289333	2.988430	-1.412240
H	-0.137337	1.130631	2.852751
H	1.044520	0.717888	-0.870886
H	-1.215932	3.238068	1.866854
H	-0.966977	4.769414	-0.259565
C	0.062525	-0.672224	1.866978
C	0.093578	-1.654765	0.776330
C	-0.489079	-1.552539	-0.468156
C	0.705141	-2.947860	0.954258
C	0.590055	-3.763780	-0.131908
S	-0.289333	-2.988428	-1.412241
H	0.137340	-1.130631	2.852751
H	-1.044514	-0.717884	-0.870888
H	1.215927	-3.238070	1.866856
H	0.966970	-4.769417	-0.259564

**C<sub>gs</sub>**

C	-1.692931	-0.394530	-1.610923
C	-1.742004	-0.338447	-0.251683
C	-0.433883	-0.363389	0.540737
C	-2.885461	-0.280404	0.623618
C	-2.581296	-0.010789	1.913391
S	-0.864389	0.223450	2.251429
H	-2.611492	-0.470052	-2.187606
H	-0.095773	-1.407514	0.640165
H	-3.903658	-0.402950	0.267499
H	-3.286003	0.088482	2.730788
C	-0.424457	-0.368686	-2.302190
C	0.717184	-0.030386	-1.642430
C	0.624758	0.434799	-0.188211
C	2.078698	-0.012336	-2.114611
C	2.999784	0.160019	-1.139663
S	2.349913	0.315525	0.494469
H	-0.390958	-0.613599	-3.360942
H	0.350844	1.502046	-0.170656
H	2.340016	-0.165486	-3.157108
H	4.074968	0.192143	-1.272226

**TS<sub>gs</sub>**

C	-0.795	2.257	-0.028
C	-1.492	0.990	0.123
C	-0.781	-0.183	0.604
C	-2.762	0.674	-0.405
C	-3.099	-0.659	-0.315
S	-1.863	-1.599	0.490
H	-1.383	3.171	-0.063
H	-0.206	-0.152	1.525
H	-3.398	1.407	-0.892
H	-3.983	-1.145	-0.705
C	0.566	2.319	-0.148
C	1.384	1.119	-0.215
C	0.790	-0.149	-0.608
C	2.678	0.966	0.327
C	3.144	-0.331	0.327
S	2.006	-1.440	-0.403
H	1.062	3.287	-0.178
H	0.217	-0.238	-1.527
H	3.239	1.790	0.757
H	4.071	-0.700	0.744

**O<sub>i</sub>**

C	-0.387203	0.629442	1.709781
C	-0.135774	1.695807	0.821197
C	0.817169	1.695635	-0.208617
C	-0.846267	2.963040	0.853157
C	-0.438040	3.841405	-0.095533
S	0.839467	3.182681	-1.093268
H	-1.159208	0.780716	2.466157
H	1.486540	0.889389	-0.472744

H	-1.628520	3.178807	1.573778
H	-0.802207	4.843351	-0.280790
C	0.345769	-0.643457	1.715215
C	0.125684	-1.699310	0.806025
C	-0.791060	-1.686790	-0.256085
C	0.834813	-2.967008	0.847670
C	0.459729	-3.834078	-0.124801
S	-0.782531	-3.163351	-1.158355
H	1.090889	-0.803521	2.496346
H	-1.451137	-0.877362	-0.533572
H	1.591673	-3.191505	1.592326
H	0.830215	-4.833891	-0.309055

**C<sub>i</sub>**

C	-1.671557	-0.484157	-1.665763
C	-1.720234	-0.421599	-0.225658
C	-0.404082	-0.445244	0.526739
C	-2.825365	-0.223695	0.596262
C	-2.531674	-0.006961	1.936517
S	-0.813379	-0.039011	2.290936
H	-2.591706	-0.677312	-2.211736
H	0.037554	-1.449125	0.525177
H	-3.843554	-0.193176	0.217985
H	-3.236519	0.198592	2.731385
C	-0.494547	-0.300767	-2.338071
C	0.713060	0.056220	-1.635115
C	0.583790	0.507344	-0.193349
C	2.031827	-0.060585	-2.063385
C	2.991343	0.175522	-1.087206
S	2.311867	0.576995	0.480031
H	-0.453326	-0.425566	-3.417347
H	0.175628	1.523319	-0.129251
H	2.299544	-0.359235	-3.073259
H	4.065189	0.106337	-1.201045

**TS<sub>i</sub>**

C	-0.028319	0.027285	-0.041862
C	0.004800	-0.002043	1.370531
C	1.242393	-0.102073	2.116950
C	-1.117714	0.182845	2.243112
C	-0.790725	0.244615	3.563924
S	0.929844	0.019672	3.847315
H	-0.978851	-0.154457	-0.539410
H	2.054992	-0.753625	1.821821
H	-2.129550	0.322902	1.875597
H	-1.450809	0.438249	4.399523
C	1.118169	0.265320	-0.820453
C	2.284552	0.863855	-0.293182
C	2.295853	1.556607	0.979199
C	3.602798	0.771543	-0.849198
C	4.574032	1.325948	-0.071678
S	3.933249	2.063191	1.390220
H	1.110043	-0.008766	-1.873505
H	1.497123	2.214878	1.296462
H	3.812321	0.250539	-1.778241
H	5.641858	1.325879	-0.248378

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