Dynamics of the Formation of a Charge Transfer State in 1,2-bis(9-anthryl)acetylene in Polar Solvents: Symmetry Reduction with the Participation of an Intramolecular Torsional Coordinate

Luis Gutiérrez-Arzaluz[1], Cesar A. Guarin[1], William Rodríguez-Córdoba[1,2], and Jorge Peon[1,*]

[1]Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, México, 04510, D.F., México.

[2]Escuela de Física, Universidad Nacional de Colombia, Sede Medellín, A.A. 3840, Medellín, Colombia

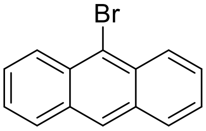
Supporting Information

1) **Detailed synthetic procedures**
2) **Steady-state emission spectra at different concentrations of BisAA in acetonitrile and cyclohexane**
3) **Full reference 27**

1) Detailed synthetic procedures

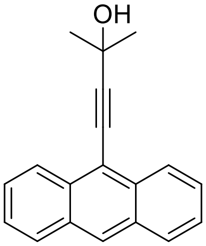
General: Reagents and solvents were purchased from Sigma-Aldrich Chemical Company. Toluene and tetrahydrofuran were dried with Linde type 4A molecular sieves and sodium wires/benzophenone, respectively. Dichloromethane and triethylamine were distilled from CaH_2 immediately before use. Except for the bromination of anthracene, all reactions were carried out under a dry N_2 atmosphere. All compounds synthesized in this study were purified by column chromatography on silica gel (100–200 mesh) using a suitable mixture petroleum ether and ethyl acetate. All physical properties and spectroscopic data agree with the values reported in the scientific literature. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Unity 300 MHz spectrometer in deuterochloroform with tretramethylsilane as internal standard. Melting points were measured on a Fisher-Johns melting point apparatus and are uncorrected. Data are reported as follows: chemical shifts (multiplicity, coupling constants, and number of protons).

9-Bromoanthracene (2).



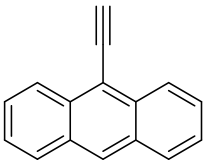
9-Bromoanthracene was synthesized following the procedure reported by Vyas et al.[1] To a stirred solution of anthracene (2.0 g, 11.2 mmol) and 1.2 equivalents of hydrobromic acid (1.1 g, of a 40% aq. solution, 13.5 mmol) in a 9:1 mixture of CH_2Cl_2:H_2O (30 mL) was slowly added 1.0 equivalent of hydrogen peroxide (1.2 g of a 30% aq. solution; 11.2 mmol) over a period of 25 min at 10–15 °C. The progress of the reaction was monitored by thin layer chromatography (TLC) and the mixture was stirred until the starting anthracene disappeared. After completion of bromination, the solvent was removed under reduced pressure and then treated with water and brine and the organic layer was extracted with ethyl acetate (3 x 20 mL). The organic layer was dried over anhydrous sodium sulphate and the product was purified by chromatography on silica gel using petroleum ether as eluent to give pure 9-bromoanthracene as a light yellow solid (2.36 g, 82%). The structure of compound **2** was characterized by various spectroscopic methods (spectra not showed) including ^{1}H NMR (200 MHz), UV–Vis and mass spectrometry (EIMS m/z 257). All spectroscopic results agree with the reported properties.

4-(Anthracen-10-yl)-2-methylbut-3-yn-2-ol(3).[2-6]



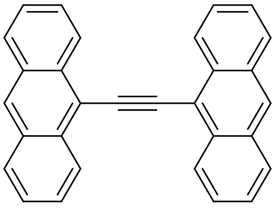
To a stirring solution of 9-bromoanthracene (5.0 g, 20.0 mmol) in 25 mL of triethylamine, 2-methylbut-3-yn-2-ol (3.28 g, 39.1 mmol), $Pd(PPh_3)_2Cl_2$(37 mg), CuI (50 mg) and PPh_3 (77.5 mg) were added. The mixturewas refluxed for 5 h under nitrogen atmosphere, cooled at room temperature and filtered. After removal of the solvent under reduced pressure, the residue was treated with dichloromethane (75 mL), washed with distilled water (3 x 20 mL) and with a salt aqueous solution of NaCl. After drying the organic layer with anhydrous Na_2SO_4, the dichloromethane was distilled off and the residual was purified by column chromatography on silica gel using petroleum ether/ethyl acetate 95:5 to yield **3** (4.5 g, 90%) as a light yellow crystalline solid. Mp 124-127 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ8.49 (d, *J*=8.72 Hz, 2H), 8.40 (s, 1H), 7.99 (d, *J*=8.33 Hz, 2H), 7.58–7.53 (m, 2H), 7.51–7.45 (m, 2H), 2.26 (s, 1H, OH), 1.84 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 132.6, 131.1, 128.6, 127.7, 126.5, 125.6, 125.7, 116.6, 105.2, 78.9, 66.2, 31.8; MS (EI) m/z 260.12.

9-Ethynylanthracene(4).[2, 5]



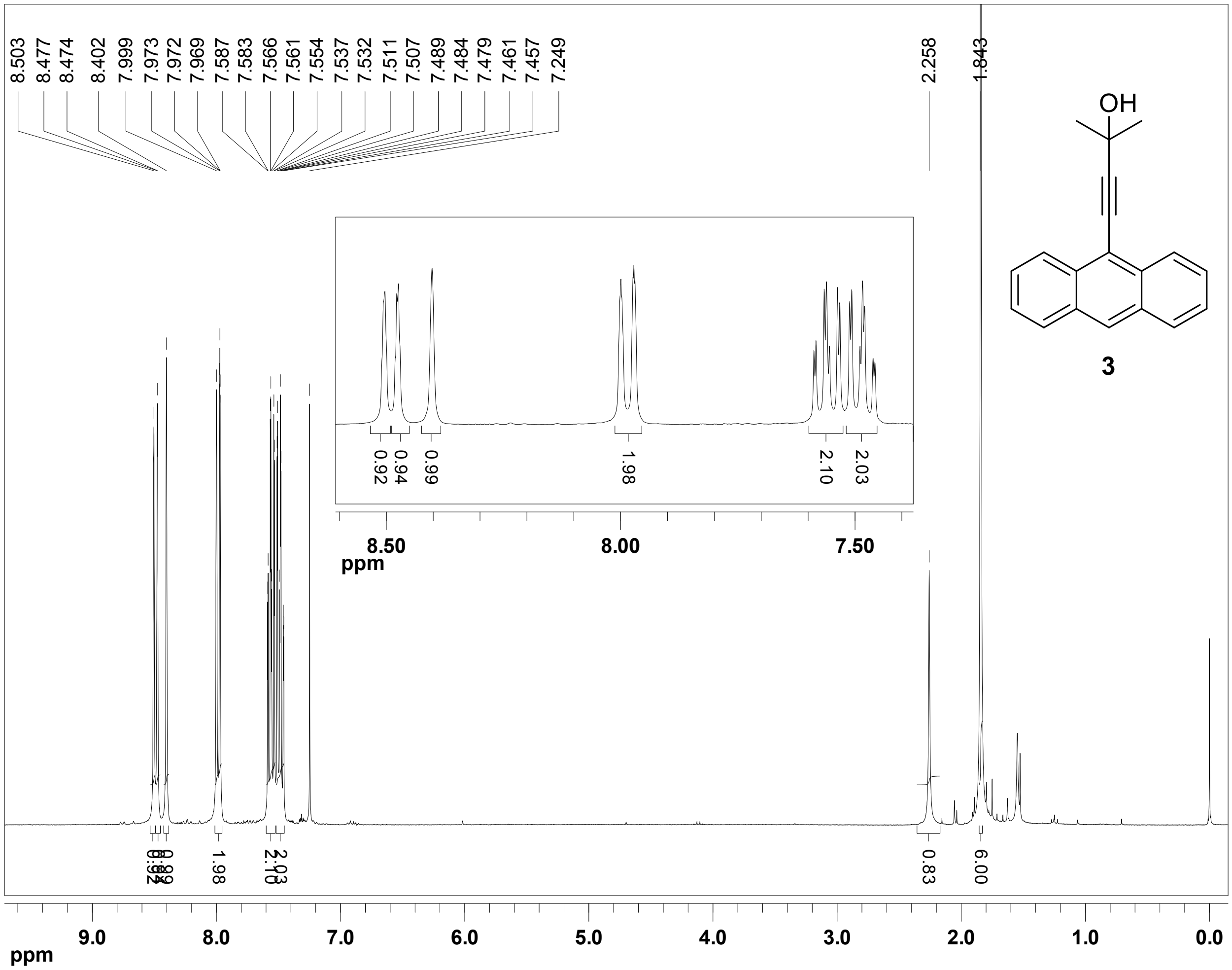
A solution of 4-(Anthracen-10-yl)-2-methylbut-3-yn-2-ol (3.0 g, 11.5 mmol) in dry toluene (100 mL) was treated with KOH (0.8 g, 14.3 mmol). The reaction mixture was heated under reflux for 25 min under nitrogen atmosphere, cooled and filtered. The solvent was removed in vacuo and the residue was purified by column chromatography using petroleum ether as eluent to yield **4** (1.9 g, 85%) as a light yellow crystalline solid. Mp 69-72 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.58 (d, *J*=8.6 Hz, 2H), 8.45 (s, 1H), 8.01 (d, *J*=8.4 Hz, 2H), 7.61–7.48 (m, 4H), 3.98 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ133.1, 131.0, 128.6, 128.2, 126.8, 126.5, 125.6, 116.0, 88.2, 80.3; MS (EI) m/z 202.08.

1,2-di(anthracen-9-yl)ethyne (5)[7-10]



9-Bromoanthracene (3.0 g, 11.6 mmol) was dissolved in dry THF (250 mL). To the solution $Pd(PPh_3)_2Cl_2$ (0.2 g), CuI (0.1 mg) and 10-Ethynylanthracene (2.1 g, 10.6 mmol) were added and the mixture was thoroughly degassed with highly-pure N_2 three times. Then, a solution of piperidine (10 mL) in 150 mL of THF was injected in one portion. The reaction mixture was heated at 70 °C for 48 h. The solvent was removed under reduced pressureand the residue was subjected to chromatography on silica gel with petroleum ether/ethyl acetate 95:5. Upon crystallization of the solid from toluene the 1,2-di(anthracen-9-yl)ethyne **5** was obtained as red-orange crystals (2.7 g, 68%). Mp >300 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ8.92 (d, *J*=8.5 Hz, 2H), 8.71 (d, *J*=8.7 Hz, 2H), 8.51 (d, *J*=6.5 Hz, 2H), 8.07 (m, 4H), 7.70–7.64 (m, 4H), 7.59–7.52 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 134.1, 131.4, 128.9, 128.3, 127.0, 126.7, 125.9, 115.9, 97.4; MS (EI) m/z 378.14

^{1}H NMR ($CDCl_3$) of 4-(anthracen-10-yl)-2-methylbut-3-yn-2-ol (**3**).



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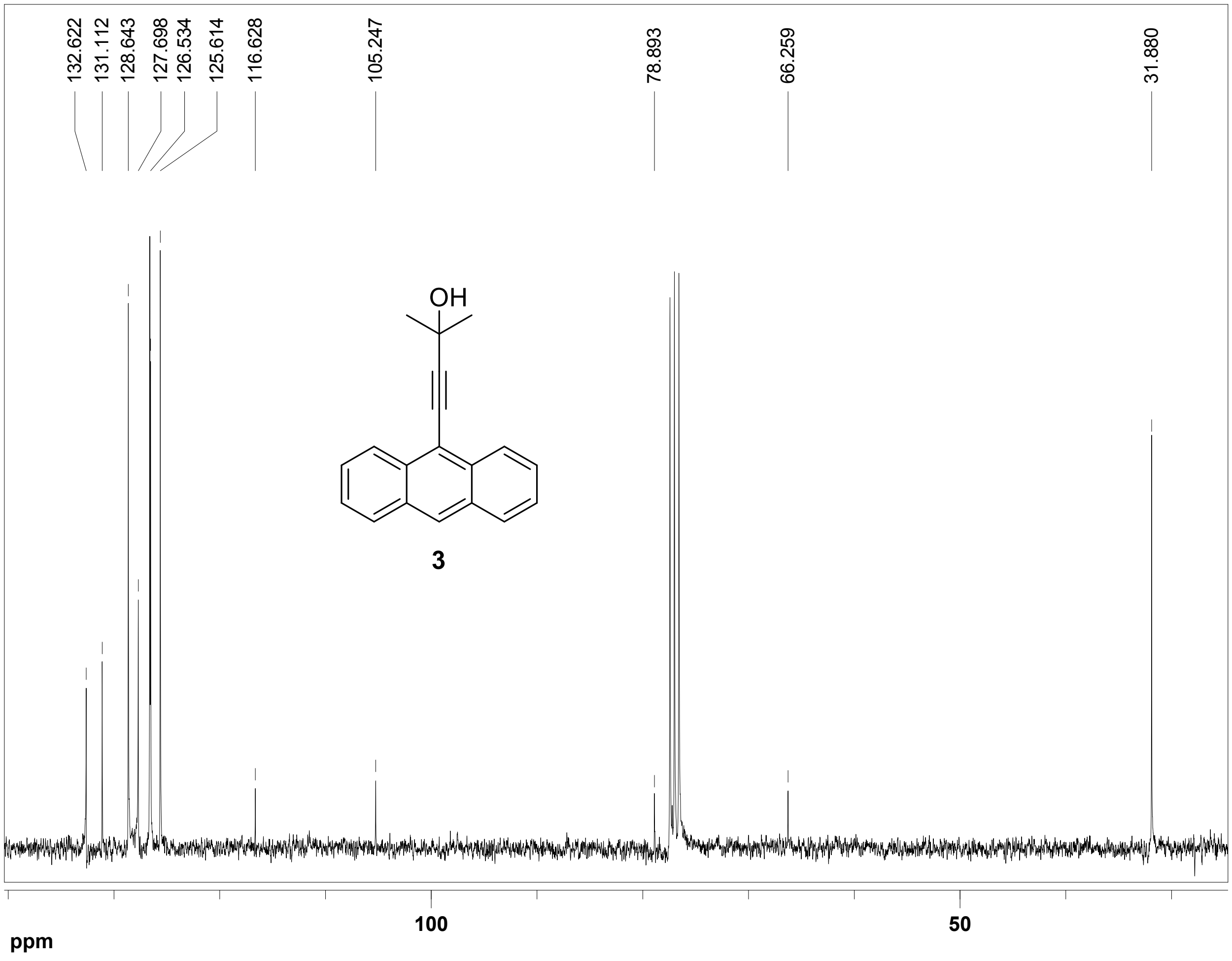
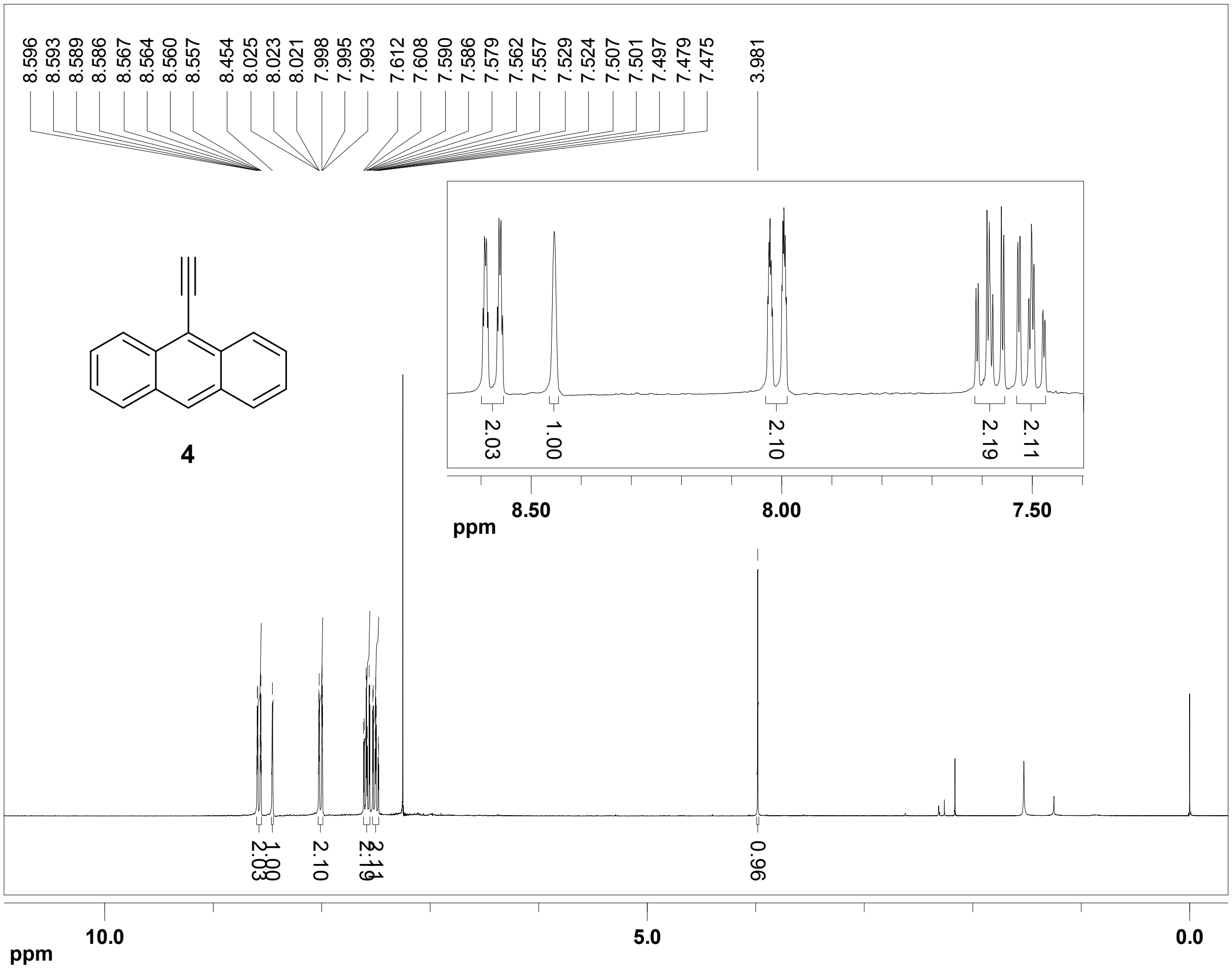
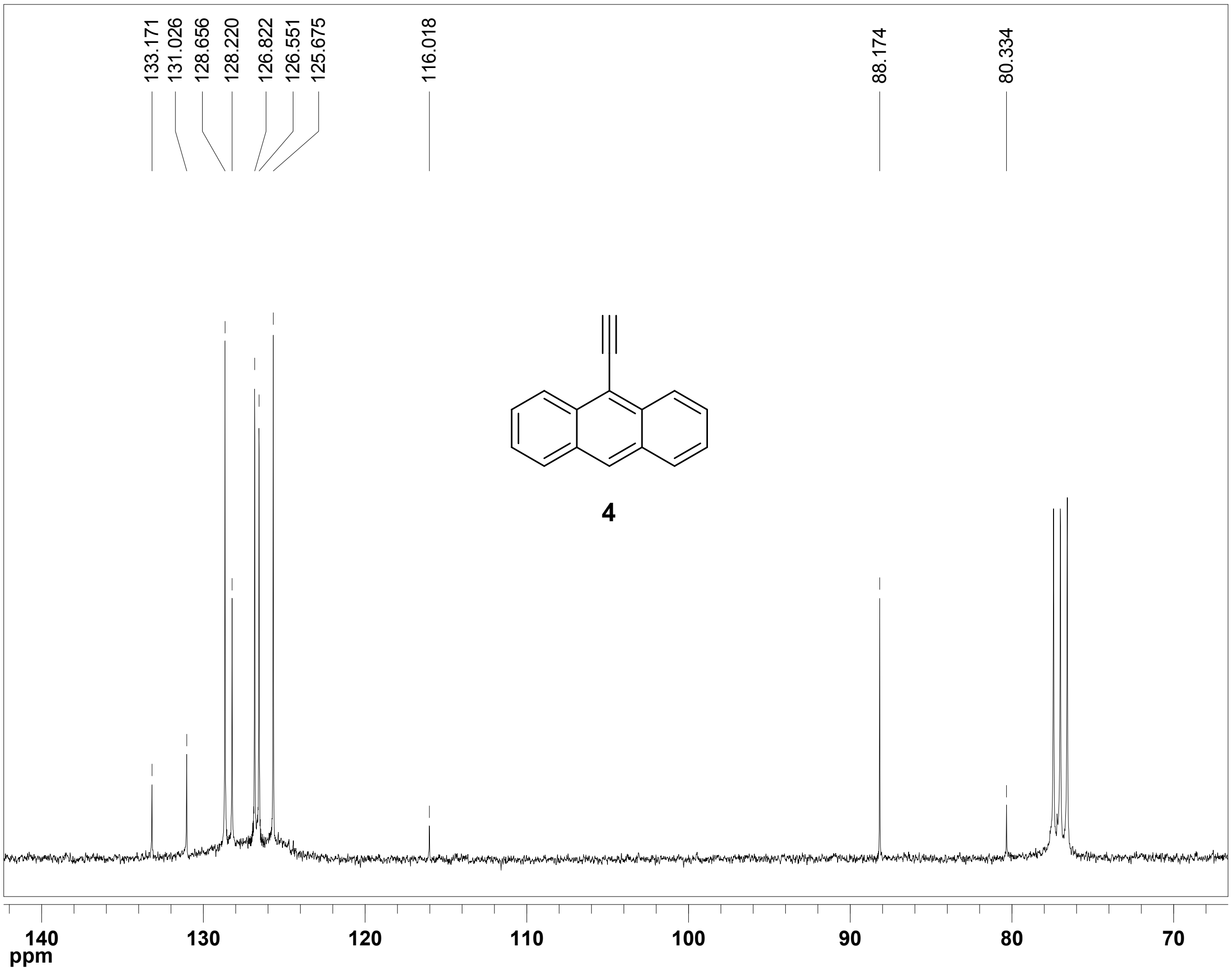
^{13}C NMR ($CDCl_3$) of 4-(anthracen-10-yl)-2-methylbut-3-yn-2-ol (**3**).



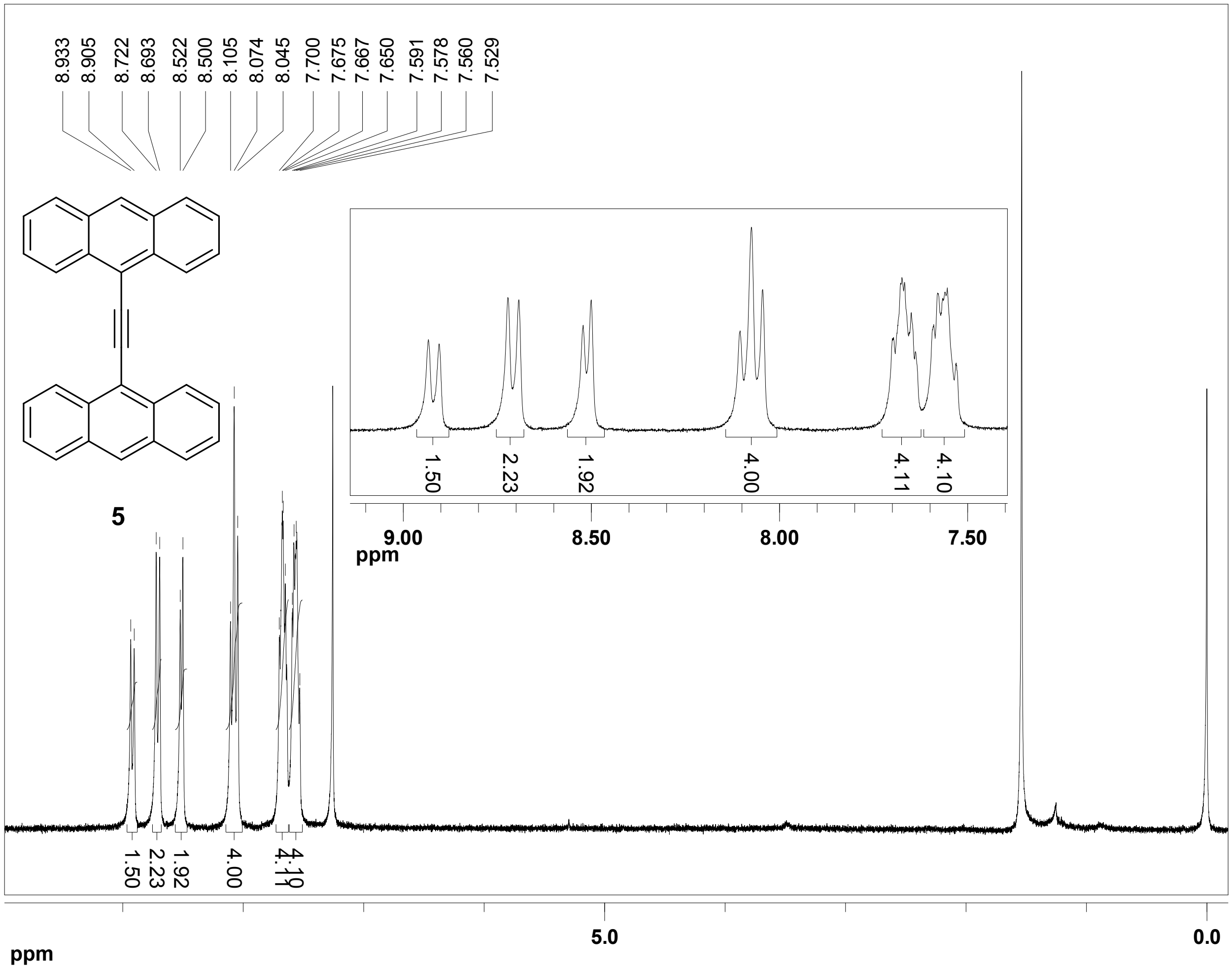
^{1}H NMR ($CDCl_3$) of 9-ethynylanthracene (**4**).



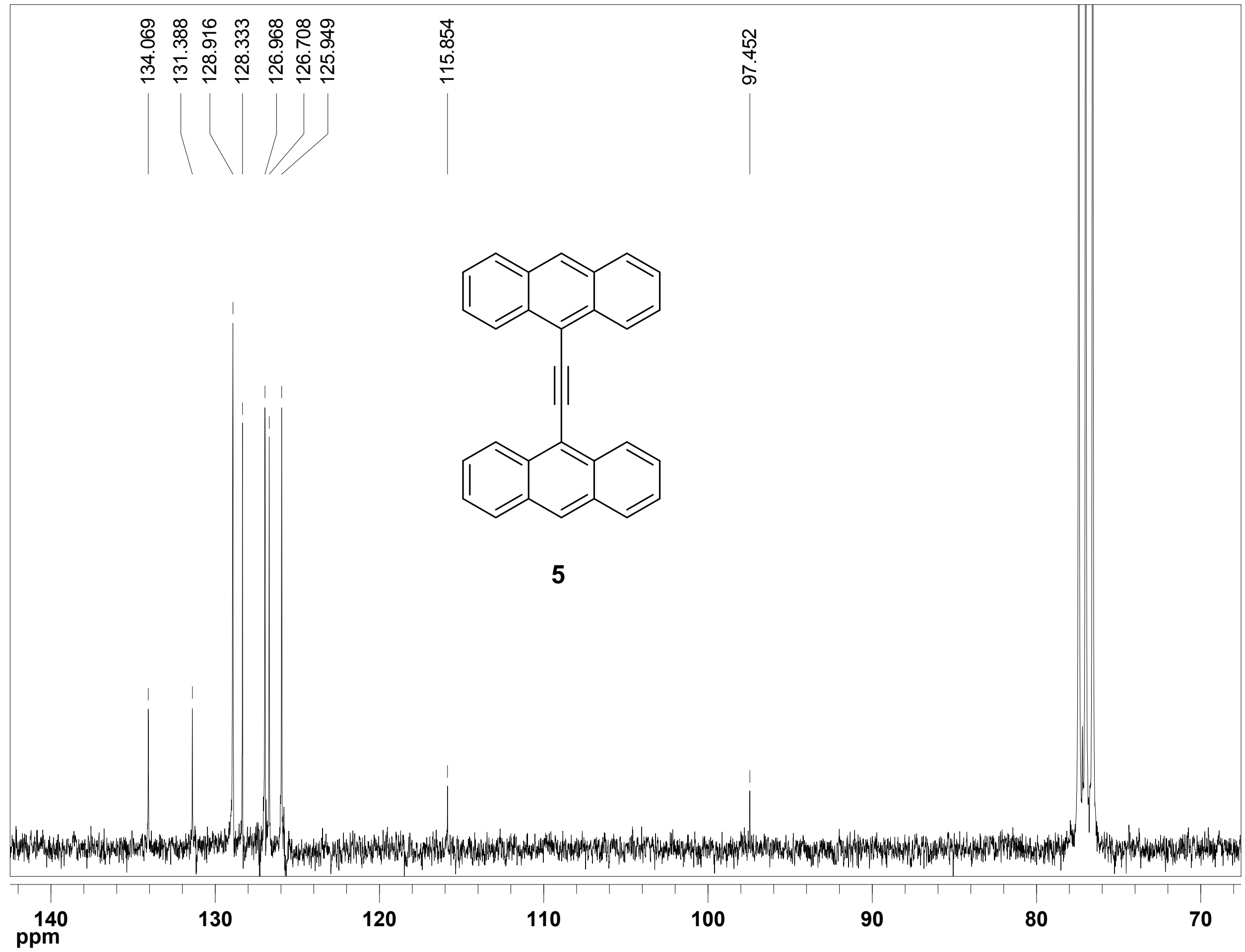
^{13}C NMR (CDCl$_3$) of 9-ethynylanthracene (**4**).



^1H NMR ($CDCl_3$) of 1,2-di(anthracen-9-yl)ethyne (**5**).



^{13}C NMR ($CDCl_3$) of 1,2-di(anthracen-9-yl)ethyne (**5**).



2) Steady-state emission spectra of BisAA at different concentrations.

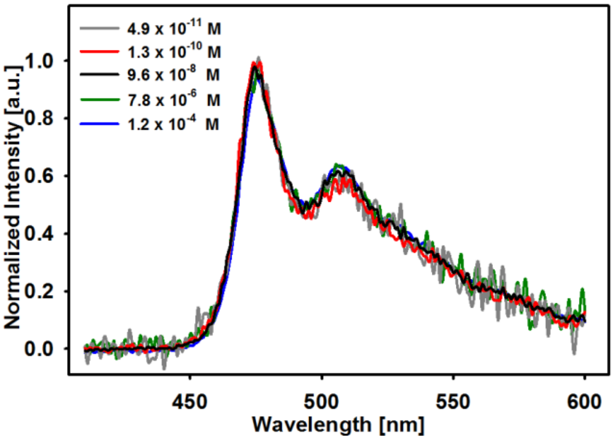


Figure S1. Steady-state emission spectra of 1,2-bis(9-anthryl)acetylene in cyclohexane at several concentrations.

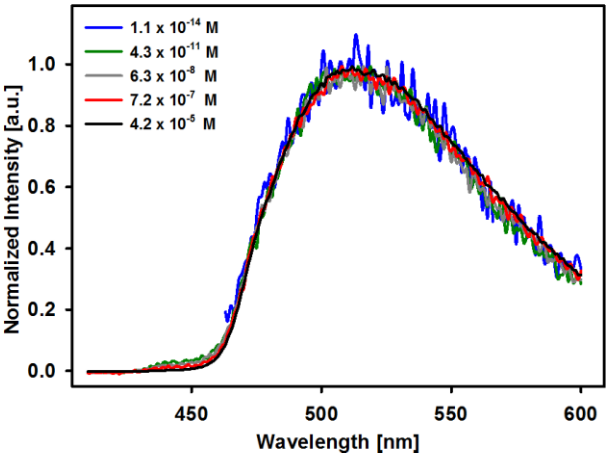


Figure S2. Steady-state emission spectra of 1,2-bis(9-anthryl)acetylene in acetonitrile at several concentrations.

3) Full Reference 27:

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