Adiabatic Ring Opening in Tethered Naphthalene and Anthracene Cycloadducts.

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Electronic Supplementary Information

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Syntheses of compounds **1** and **3** and the corresponding cycloadducts were accomplished following literature procedures.^{1, 2} Synthesis of **2** and **c2** were completed following the procedure reported for **1** and **c1**, respectively. Compounds **4**, **5**, **c4** and **c5** were provided as generous gifts from Sigma Aldrich Fine Chemicals (SAFC).

Absorption and emission measurements were performed at room temperature (298 K) in argon saturated acetonitrile. Absorption spectra were recorded on a Shimadzu UV-2401 PC spectrometer and emission spectra were recorded with a FluoroLog 3 spectrometer (Horiba), with continuous stirring during the acquisition. A fresh (unexposed) solution of the cycloadduct was used for each absorption or emission experiment to avoid interference from photoproducts formed during the measurement.

Synthesis of 2.



Scheme S1. Synthesis of 2.

A solution of 1-acetonaphthone (1.05 equiv) and 4-methoxy-1-naphthaldehyde (1 equiv) was prepared in absolute ethanol. With stirring sodium hydroxide pellets (1.1 equiv) were added and stirring continued for 2 hours. The yellow precipitate was mixed thoroughly during the reaction. The solution was diluted with water ($\sim 50 \text{ mL} / 10 \text{ mL}$ ethanol) and the resulting solid was collected by filtration and recrystallized from ethanol.

The chalcone (3-(4-methoxynaphthalen-1-yl)-1-(naphthalen-1-yl)prop-2-en-1-one) was dissolved in ethanol and reduced with 5 wt% palladium on carbon in the presence of hydrogen. After the absence of the starting material was confirmed by TLC analysis (20 % chloroform in hexane), the catalyst was filtered off, the solvent was evaporated and the residue was used without further purification. The intermediate ketone (3-(4-methoxynaphthalen-1-yl)-1-(naphthalen-1-yl)propan-1-one) was heated to ~ 180 °C with potassium hydroxide and excess of hydrazine hydrate in ethylene glycol for about 4 hours. The product was extracted with chloroform and purified by column chromatography using hexanes and toluene as eluants. ¹H NMR spectra of **2** is shown in Figure S1.

Synthesis of c2.



Scheme S2. Synthesis of c2.

A solution of **2** (5 mM in methylcyclohexane) was bubbled with argon for 30 min in a pyrex flask and was irradiated using a Rayonet reactor with 300 nm lamps. Argon bubbling was continued during the irradiation. After complete conversion, the solvent was evaporated under vacuum at < 40 °C to isolate the cycloadduct as a solid. It was purified by column chromatography (30 – 40 % chloroform in hexanes. ¹H NMR spectra of **c2** is shown in Figure S1.



Figure S1. ¹H NMR spectra (500 MHz) of 2 (bottom) and c2 (top) recorded in CDCl₃.

Emission spectra of 1 and c1 recorded at 77 K.



Figure S2. Emission spectra of 1 (solid line) and c1 (dashed line) recorded at 77 K in methylcyclohexane. λ_{ex} (1) = 273 nm; λ_{ex} (c1) = 264 nm.



Figure S3. A: Emission spectra of **2** (solid line) and **c2** (dashed line) recorded at 295 K in acetonitrile (MeCN); $\lambda_{ex} = 272$ nm. B: Emission spectra of **2** recorded at 295 K (solid line) and at 77 K (dashed line) in methylcyclohexane (MCH); $\lambda_{ex} = 283$ nm. C: Emission spectra of **c2** recorded at 295 K (solid line) and at 77 K (dashed line) in MCH; $\lambda_{ex} = 272$ nm.

Emission spectra of 4, c4, 5 and c5 at 295 K.



Figure S4. Emission spectra of **4** (solid line) and **c4** (dashed line) recorded in acetonitrile at 295 K; $\lambda_{ex} = 255$ nm; $abs^{255nm} = 0.19$.



Figure S5. Emission spectra of **5** (solid line) and **c5** (dashed line) recorded in MeCN at 295 K; $\lambda_{ex} = 255 \text{ nm}$; $abs^{255nm} = 0.20$.

Reference

- 1. E. A. Chandross and C. J. Dempster, Intramolecular excimer formation and fluorescence quenching in dinaphthylalkanes, *J. Am. Chem. Soc.*, 1970, **92**, 3586-3593.
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