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Supporting Information

Light-triggered assembly-disassembly of an ordered donor-acceptor π -stack using a photoresponsive dimethyldihydropyrene π -switch

V. Siva Rama Krishna,^a Mousumi Samanta,^a Suman Pal,^a N.P. Anurag^a and Subhajit Bandyopadhyay^{*a}

Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Kolkata, Mohanpur, Nadia WB 741246, India

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1. Experimental section

1, 4, 5, 8-naphthalenetetracarboxylic acid dianhydride (NDA) and other reagents were purchased from Sigma Aldrich and was used without further purification. Reactions were monitored with thin layer chromatography using Merck plates (TLC Silica Gel 60 F254). Developed TLC plates were visualized with UV light (254 nm and 366 nm), and/or iodine. Silica gel (100-200 mesh, Merck) was used for column chromatography. All reactions were carried out under an inert atmosphere of nitrogen or argon. The ¹H and ¹³C NMR spectra were recorded on a 400 MHz Jeol instrument and 500 MHz Bruker instruments. Chemical shifts are reported in δ values relative to the solvent peak for ¹H and ¹³C NMR spectra, except where noted otherwise. Peak splitting patterns in the NMR are reported as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; and br, broad. Mass spectrometric data were obtained on an Acquity[™] Ultra Performance LC. Absorption and fluorescence measurements were recorded with 3 mL quartz cuvettes (Helma) having an optical path length of 10 mm. Final concentrations of the components have been mentioned in the main text or below the figures. The molar absorptivity values of the species were determined from the data obtained at five different concentrations. UV-Vis spectra and the kinetics were monitored using a Cary400 Bio UV-Vis spectrophotometer. Steady state fluorescence data were recorded with Horiba Jobin Yvon (Fluoromax-3, Xe-150 W, 250-900 nm) spectrofluorimeter with the solvents and the excitation and emission slits as mentioned in the text. DLS experiments were done on a Malvern Zetasizer Nano ZS instrument equipped with a HeNe laser of 4.0 mW operating at λ =633 nm. SEM sample images were recorded on Carl Zeiss Supra 55VP field emission scanning electron microscope (FE-SEM) with an energy-dispersive X-ray spectroscopic (EDS) attachment.

Synthesis:

NDHP was synthesized according to the literature procedure as reported by Mitchell and coworkers.¹

2, 7-Di-t-butyl-trans-14c,14d-dimethyl,14c,14d-di-hydrodibenzo[de,qr]napthacene (NDHP)

The naphtho-adduct¹ (400 mg, 0.9 mmol) and Fe₂(CO)₉ (520 mg, 1.43 mmol) in benzene (50 mL) were refluxed for 3 hours under inert argon atmosphere in the dark. Then the reaction mixture was filtered through deactivated silica gel and eluted with the benzene (90 mL). The eluted purple solution was evaporated in the dark, re-evaporated and the residue was purified by column chromatography using hexane/CH₂Cl₂ (6:1) as eluant over silica gel (deactivated with 5% water) to obtain 303 mg of the product (76%). mp (dec) $173-175^{\circ}C$; ¹H NMR (CDCl₃) δ 8.98 (s, 2, H-9,14), 8.09 (AA'XX', 2, *J*_{10,11}=8.30 Hz, *J*_{10,12}=1.20 Hz, *J*_{10,13}=0.83 Hz, 8.01 2, H-1,8), 7.56 H-10,13), (d, J=1.3 Hz, (AA'XX', 2, J_{11,12}=6.66 Hz, J_{11,13}=1.20 Hz, H-11,12), 6.86 (d, J=1.3 Hz, 2, H-3,6), 6.67 (s, 2, H-4,5), 1.46 (s, 18, C(CH₃)₃), -0.54 (s, 6, CH₃); ¹³C NMR (CDCl₃) δ 144.6, 139.2, 135.7, 131.4, 128.6, 127.6, 125.6, 122.6, 121.1, 119.9, 117.6, 37.7, 35.1, 30.2, 19.2; MS m/z 444.2807 (MH⁺).

c-NDHP: ¹H NMR (CD₃OD) δ 9.35 (s, 2H), 8.18 (s, 4H), 7.58-7.56 (dd, *J*=3.04 Hz, 2H), 6.94 (s, 2H), 6.74 (s, 2H), 1.42 (s, 18, C(CH₃)₃), -0.71 (s, 6, CH₃).

o-NDHP : ¹H NMR (CD₃OD) δ 8.29, 8.01-7.91 (m), 7.74-7.61 (m), 7.30 (d, J = 2 Hz), 7.24 (d, J = 2 Hz), 6.82 (s), 1.73 (s, CH3), 1.57 (s, (C(CH3)3)).

2. UV-Visible spectra of *c*-NDHP and NDA

All titrations and equilibrium measurements were performed at a temperature mentioned in the figure captions. Excitations were done at **320** nm with 5/5 nm slit width.



Figure S1. Absoption spectra of NDA (10 µM) in methanol



Figure S2. Photoisomerisation of NDHP: Absorption spectra of *c*-NDHP (black line) and *o*-NDHP (red line) obtained after exposure to visible light (> 490 nm). The process can be reversed on exposure to 366 nm UV light.



Figure S3. UV-visible spectra of *c*-NDHP (10 μM, red line), NDA (10 μM, black line), 1:1 ratio of *c*-NDHP and NDA (blue line) and an 1:1 ratio of *c*-NDHP and NDA upon exposure to visible light (0 to 600 s).

3. Dynamic light scattering (DLS) experiments



Figure S4. DLS images of a) *c*-NDHP and b) NDA in 99:1 (v/v) methanol/DMSO.

4. Job's plot ²



Figure S5. Job's plot for the determination of the stoichiometry of the interaction between c-NDHP and NDA from the ¹H NMR chemical shift values. The total concentration of c-NDHP and NDA was kept constant at 1 mM for the experiment.

5. Computational studies

Geometry optimization was performed by DFT using B3LYP/ G(d) level theory by using Gaussian 09.



Figure S6. a) HOMO of *c*-NDHP, the dotted area shows where the site where the NDA interacts; b) LUMO of NDA and c) electronic distribution stacking of 1:1 *c*-NDHP and NDA.





7. ¹³C NMR spectrum of NDHP



8. Mass spectrum of NDHP



9. References

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