Supporting Information

Photoinduced Intramolecular Charge Transfer in a Cross-Conjugated Push-Pull Enediyne: Implications toward Photoreaction

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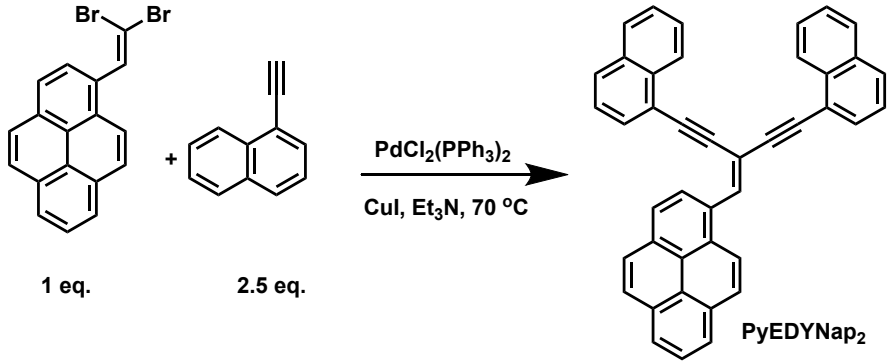
General Experimental Procedure for Synthesis:

Melting point of the push-pull enediynyl dye **PyEDY(PhNMe$_2$)$_2$** was recorded using Sigma melting point apparatus in capillary tubes. This value was uncorrected. IR spectrum of the dye was measured using JASCO FT-IR-4100 spectrometer. ^{1}H (500 MHz) and ^{13}C (100 MHz) NMR spectra of the derivative were recorded on Bruker Avance 500 spectrometer. 500 MHz NMR Bruker Avance spectrometer was used for photocyclization reaction. The chemical shifts (δ ppm) and coupling constants (Hz) from the NMR spectra were calculated with reference to chloroform. In the ^{13}C NMR spectra, the nature of the carbons (C, CH, CH_2 or CH_3) was confirmed through recording DEPT-135 experiment. High resolution mass measurement of the dye was carried out using Micromass Q-ToF ESI instrument with direct inlet mode. Analytical thin-layer chromatography (TLC) were done on glass plates (7.5 x 2.5 and 7.5 x 5.0 cm) coated with Acme's silica gel G containing 13% calcium sulfate as binder or on pre-coated 0.2 mm thick Merck 60 F_{245} silica plates. A combination of ethyl acetate and hexane was used as eluent. Visualization of the spots on the TLC plates was done by UV-

chamber and then exposure to iodine vapor. The dye **PyEDY(PhNMe$_2$)$_2$** was thoroughly purified using silica gel [Acme's silica gel (100–200 mesh)] column chromatography.

The synthesis and characterization of the dye **AnEDYNap$_2$** are provided in our earlier publication.[1] The synthetic characterization of **PyEDYNap$_2$** was made in a similar way to the push-pull dye **PyEDY(PhNMe$_2$)$_2$**.



Scheme S1. Synthesis of **PyEDYNap$_2$** using Sonogashira reactions.

4,4'-(3-(pyren-1-ylmethylene)penta-1,4-diyne-1,5-diyl)bis(N,N-dimethylaniline) (PyEDY(PhNMe$_2$)$_2$)

Physical appearance: yellow solid

m.p.: 168-170 ^{o}C

IR (neat): 2981, 2370, 2325, 2173, 1648, 1611, 1517, 1411, 1352, 1184, 847, 716, 639 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ 9.07 (d, 1H), 8.44 (d, 1H), 8.19 (d, 4H), 8.13 (d, 2H), 8.06 (s, 1H), 8.01 (dd, 1H), 7.51 (d, 2H),7.37 (d, 2H), 6.70 (d, 2H), 6.63 (d, 2H), 2.99 (s, 12H).

^{13}C NMR (100 MHz, CDCl$_3$, DEPT): δ 150.36 (1 x C), 150.29 (1 x C), 137.15 (1 x CH), 133.11 (1 x C), 133.05 (2 x CH), 131.51 (1 x CH), 131.03 (1 x CH), 130.69 (1 x C), 129.06 (1 x C), 127.84 (1 x CH), 127.78 (1 x CH), 127.61 (1 x CH), 126.55 (2 x CH), 126.07 (1 x CH), 125.57 (1 x C), 125.42 (1 x CH), 125.01 (2 x C), 124.98 (1 x CH), 124.51 (1 x CH), 123.47 (1 x C), 111.98 (1 x C), 111.90 (1 x C), 110.04 (2 x CH), 109.91(2 x CH), 106.50 (1 x

C), 95.06 (1 x C), 90.26 (1 x C), 88.38 (1 x C), 86.26 (1 x C), 40.37 (2 x CH_3), 40.30 (2 x CH_3).

HRMS (ESI, M+H$^+$): m/z calcd. for $C_{38}H_{30}N_2$ 514.24, found 514.2494.

1-(4-(naphthalen-1-yl)-2-(naphthalen-1-ylethynyl)but-1-en-3-ynyl)pyrene (PyEDYNap$_2$):

Physical appearance: yellow solid

m.p.: 158-160 ^oC

IR (neat): 3083, 2922, 2854, 2203, 2136, 1633, 1596, 1459, 1439, 1028, 842, 750, 684 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.10 (d, 1H), 8.68 (d, 1H), 8.45 (d, 1H), 8.34 (s, 1H), 8.27 (d, 1H), 8.19 (d, 1H), 8.12 (d, 1H), 8.10 (d, 2H), 8.08 (dd, 4H), 7.91 (t, 2H), 7.83 (d, 1H), 7.76 (d, 1H), 7.70 (t, 1H), 7.91 (t, 1H), 7.60 (t, 1H), 7.55-7.42 (m, 3H), 7.34 (t, 1H).

^{13}C NMR (100 MHz, $CDCl_3$, DEPT): δ 140.40 (1 x C), 133.64 (2 x C), 133.47 (1 x C), 133.41 (1 x C), 133.26 (1 x C), 132.15 (1 x CH), 131.46 (1 x CH), 131.03 (1 x CH), 130.99 (1 x CH), 130.74 (1 x CH), 130.02 (1 x CH), 129.36 (1 x C), 129.23 (1 x CH), 128.52 (1 x CH), 128.32 (1 x CH), 127.57 (1 x CH), 127.14 (1 x CH), 126.98 (1 x C), 126.75 (1 x CH), 126.68 (1 x CH), 126.60 (1 x CH), 126.48 (1 x CH), 126.42 (1 x CH), 126.26 (1 x CH), 125.92 (1 x CH), 125.77 (1 x CH), 125.49 (1 x CH), 125.45 (1 x C), 125.42 (1 x C), 125.38 (1 x C), 124.99 (1 x CH), 124.89 (1 x CH), 124.69 (1 x CH), 123.34 (1 x CH), 120.78 (1 x C), 120.66 (1 x C), 105.96 (1 x C), 94.75 (1 x C), 92.34 (1 x C), 92.20 (1 x C), 87.67 (1 x C).

HRMS (ESI, M+Na$^+$): m/z calcd. for $C_{42}H_{24}$ 528.19, found 528.1779.

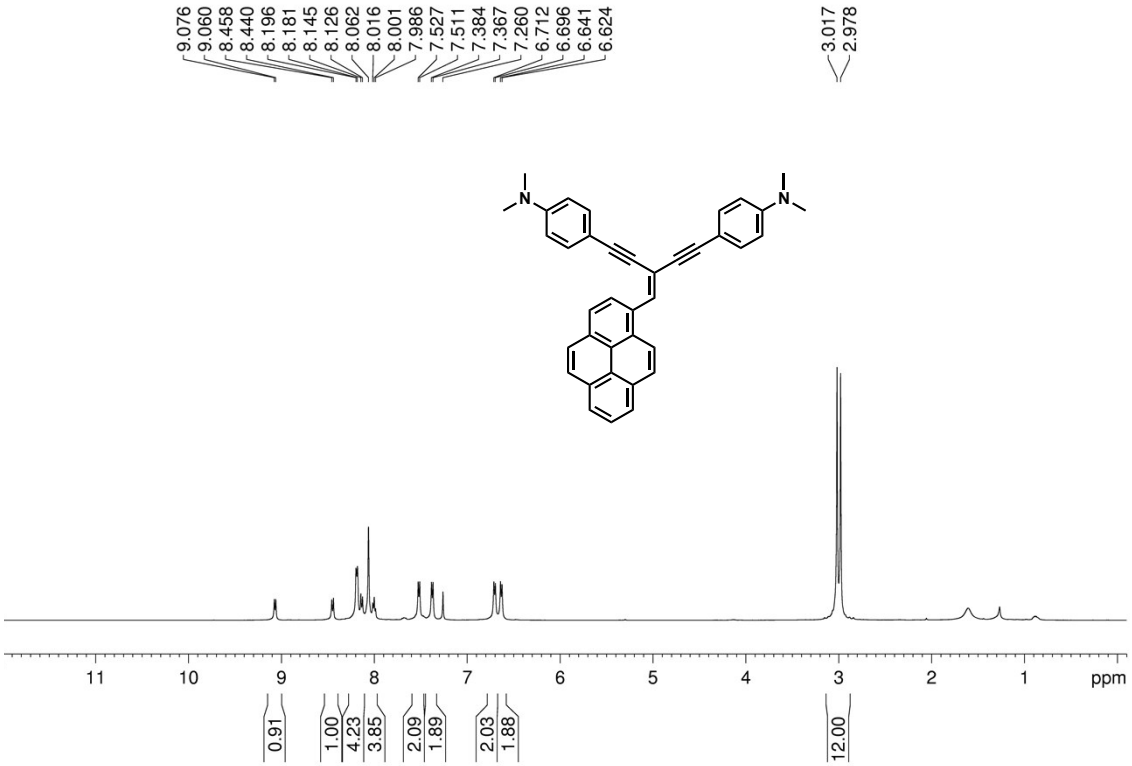


Figure S1. ^{1}H NMR spectrum of **PyEDY(PhNMe$_2$)$_2$** in $CDCl_3$ (500 MHz).

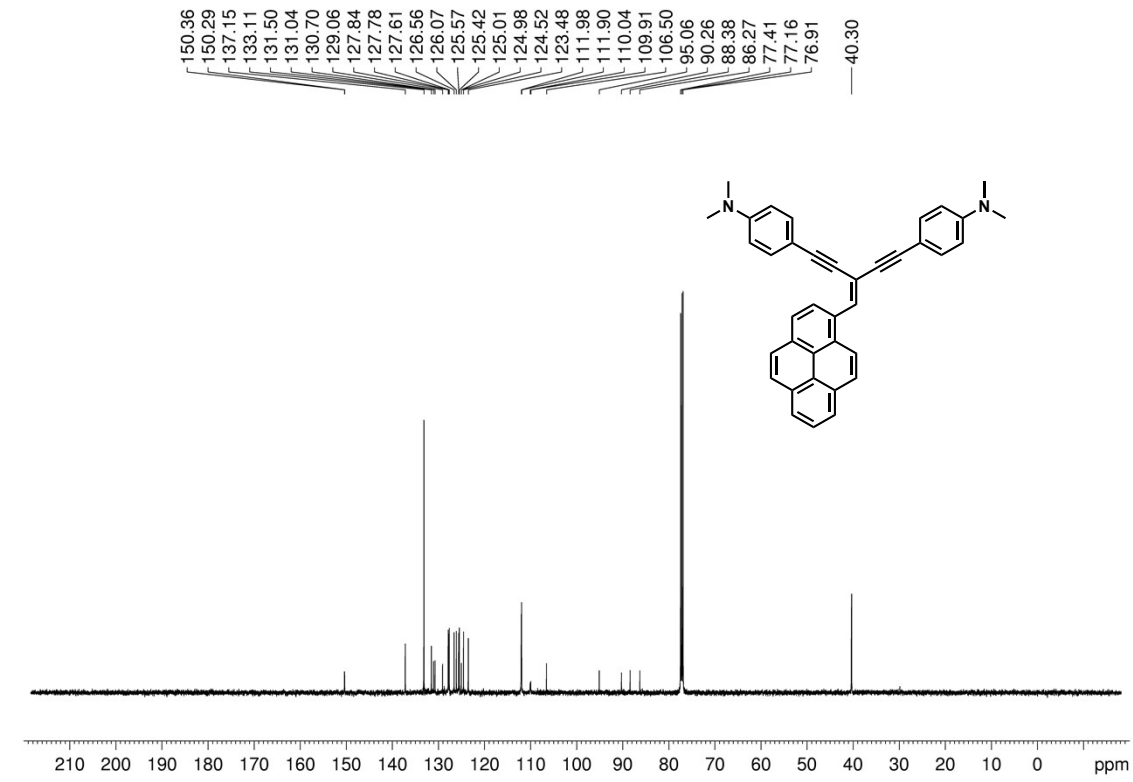


Figure S2. ^{13}C NMR spectrum of **PyEDY(PhNMe$_2$)$_2$** in $CDCl_3$ (100 MHz).

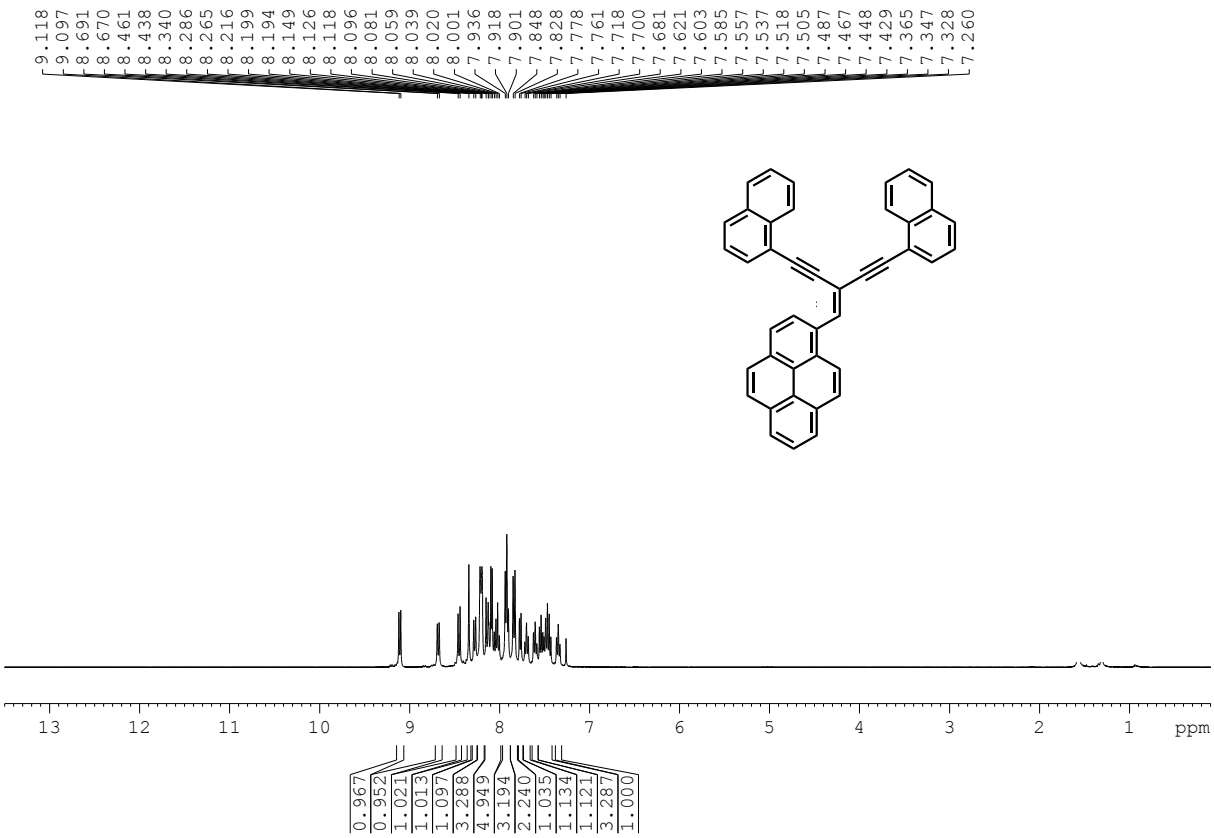


Figure S3. ^{1}H NMR spectrum of **PyEDYNap$_2$** in $CDCl_3$ (500 MHz).

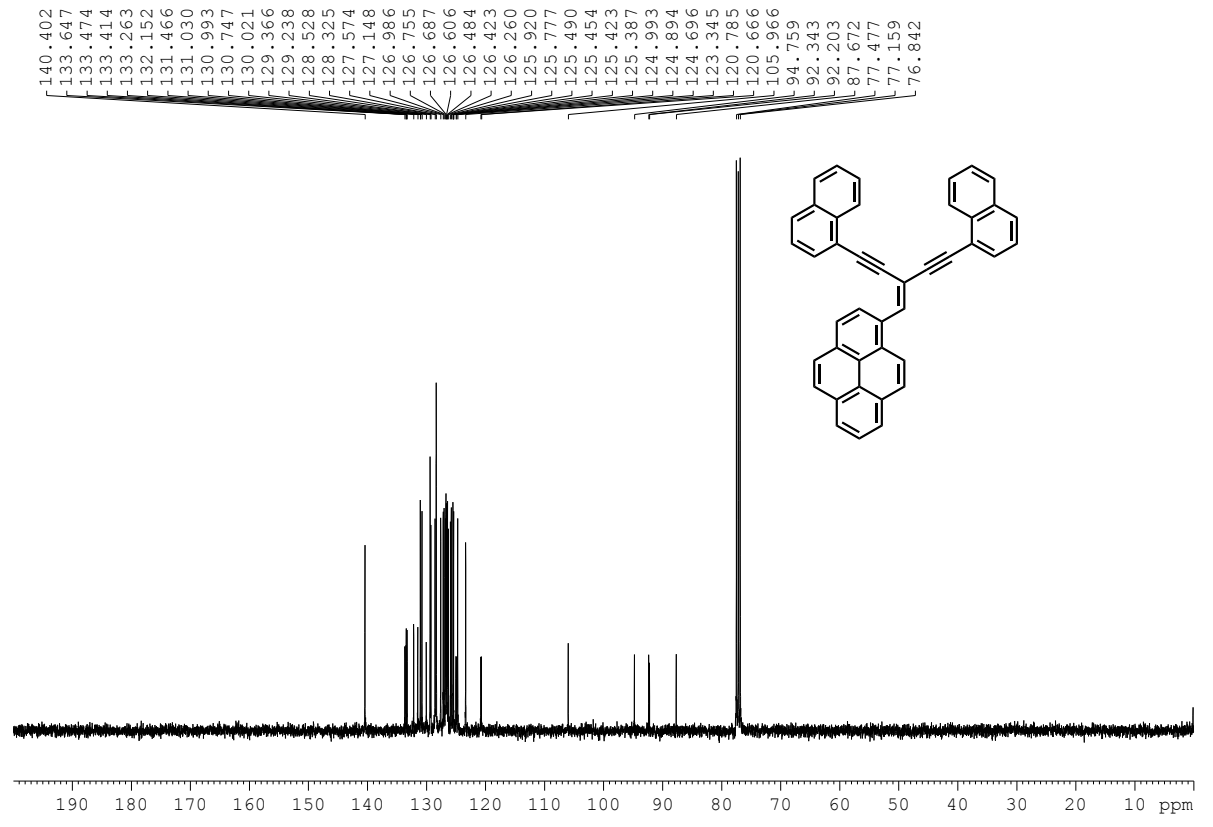


Figure S4. ^{13}C NMR spectrum of **PyEDYNap$_2$** in $CDCl_3$ (100 MHz).

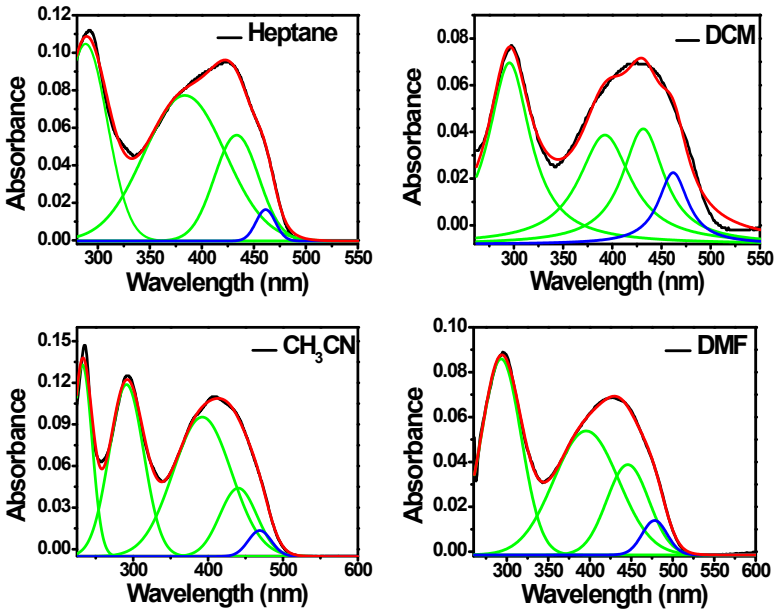


Figure S5. Gaussian fitting of absorption spectra of **PyEDY(PhNMe$_2$)$_2$** in some representative solvents with varying polarities (c = 1 x 10^{-6} M).

Table S1. Vertical absorption wavelength (λ_{abs}), oscillator strength (f), and orbital contributions of **PyEDY(PhNMe$_2$)$_2$** using PBEO/6-311+g(d,p) in different solvents. 'H' represents highest occupied molecular orbitals (HOMO) and 'L' represents lowest unoccupied molecular orbitals (LUMO).

Solvents	**PyEDY(PhNMe$_2$)$_2$**			
	λ_{abs} (nm) expt	PBEO/6-311+g(d,p)		
		λ_{abs} (nm)	f	Orbital Transition (%)
Heptane	461	480	0.739	H→L (98)
Cyclohexane	463	481	0.749	H→L (98)
Dioxane	466	482	0.747	H→L (98)
THF	461	484	0.742	H→L (98)
DCM	462	485	0.748	H→L (97)
iPrOH	465	485	0.737	H→L (97)
MeOH	466	484	0.724	H→L (97)
CH_3CN	469	485	0.729	H→L (97)
DMF	478	486	0.754	H→L (97)

Table S2. Photophysical parameters, quantum yield and rate constants of **PyEDY(PhNMe$_2$)$_2$** in different solvents (λ_{ex} longest absorption wavelength and λ_{em} shorter wavelength band of the structured emission band has been taken).

Solvents	**PyEDY(PhNMe$_2$)$_2$**							
	λ_{abs} (nm)	λ_{em} (nm)	Stokes shift (cm^{-1})	ε (x 10^4) $M^{-1}cm^{-1}$	ϕ	τ (ns)	K_r (10^8 s^{-1})	K_{nr} (10^8 s^{-1})
Cyclohexane	463	483	894	10.1	0.66	1.7	3.6	1.8
Dioxane	466	508	1774	10.4	0.15	0.8	2.1	12.1
THF	461	546	3376	10.3	0.10	1.1	0.9	8.2
DCM	462	547	3359	10.5	0.10	0.6	2.0	18.0
iPrOH	465	542	3055	11.7	0.12	0.9	1.5	11.0
MeOH	466	565	3760	9.6	0.05	0.5	1.0	19.0
CH_3CN	469	593	4458	10.7	0.03	0.9	0.38	12.1
DMF	478	600	4254	11.6	0.02	0.7	0.40	19.6

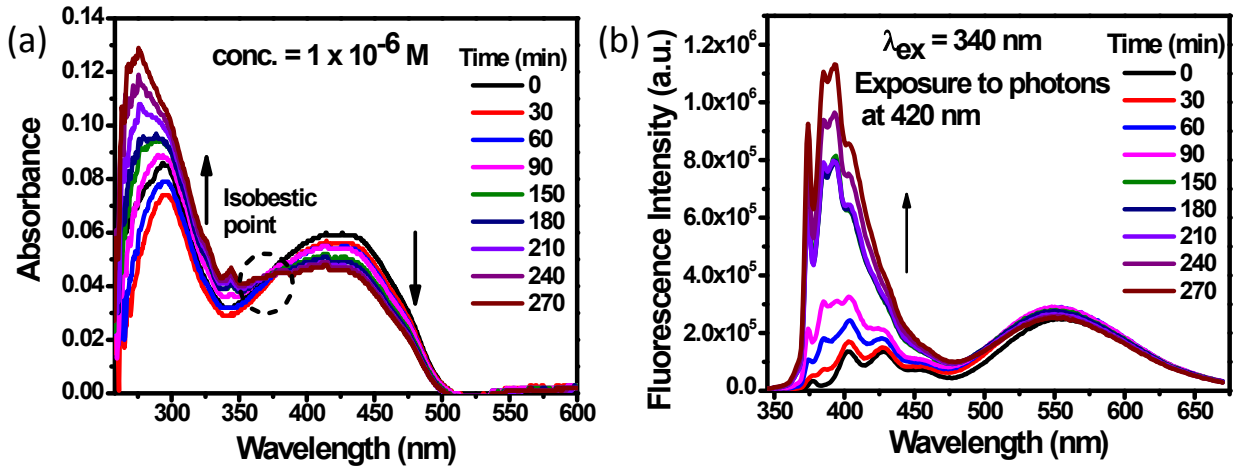


Figure S6. Steady-state (a) UV–visible absorption and (b) emission spectra of **PyEDY(PhNMe$_2$)$_2$** in THF (c = 1 x 10^{-6} M, λ_{ex} = 340 nm) when irradiated at 420 nm for 270 minutes at the interval of 30 minutes in the presence of air.

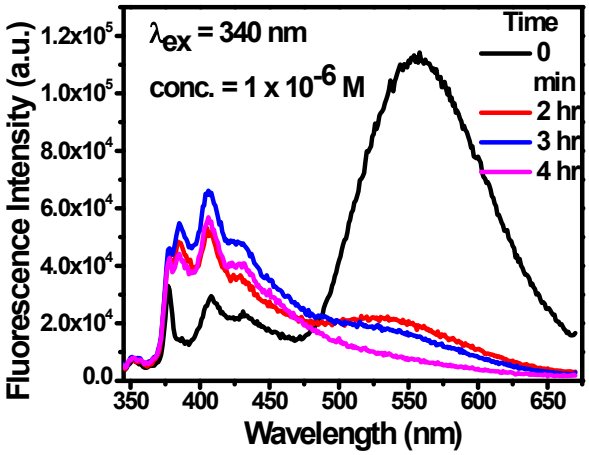


Figure S7. Steady-state emission spectra of **PyEDY(PhNMe$_2$)$_2$** in THF (c = 1 x 10^{-6} M, λ_{ex} = 340 nm) when irradiated under sunlight for 4 hours.

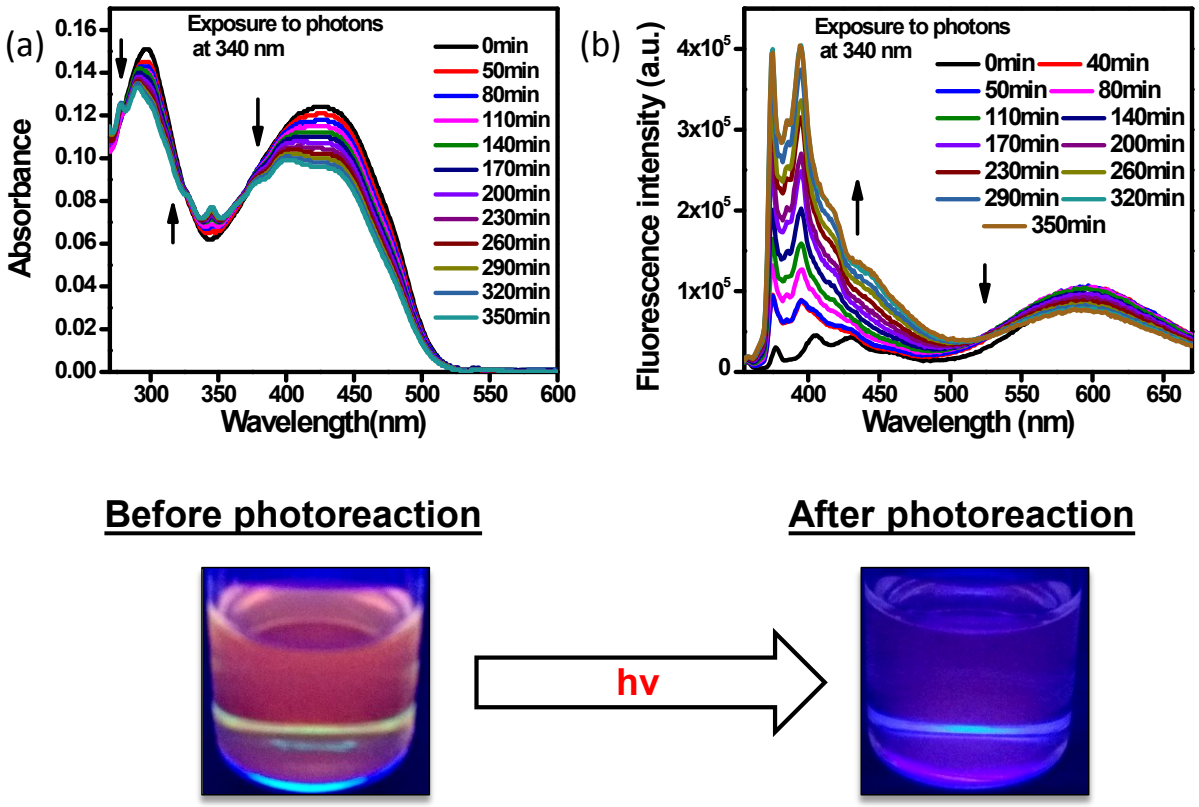


Figure S8. Steady-state (a) UV–visible absorption and (b) emission spectra of **PyEDY(PhNMe$_2$)$_2$** in DMF (c = 1 x 10^{-6} M, λ_{ex} = 340 nm) when irradiated at 340 nm for 350 minutes at the interval of 30 minutes in the presence of air. Photograph of **PyEDY(PhNMe$_2$)$_2$** in DMF under 365 nm UV lamp taken before and after photoreaction.

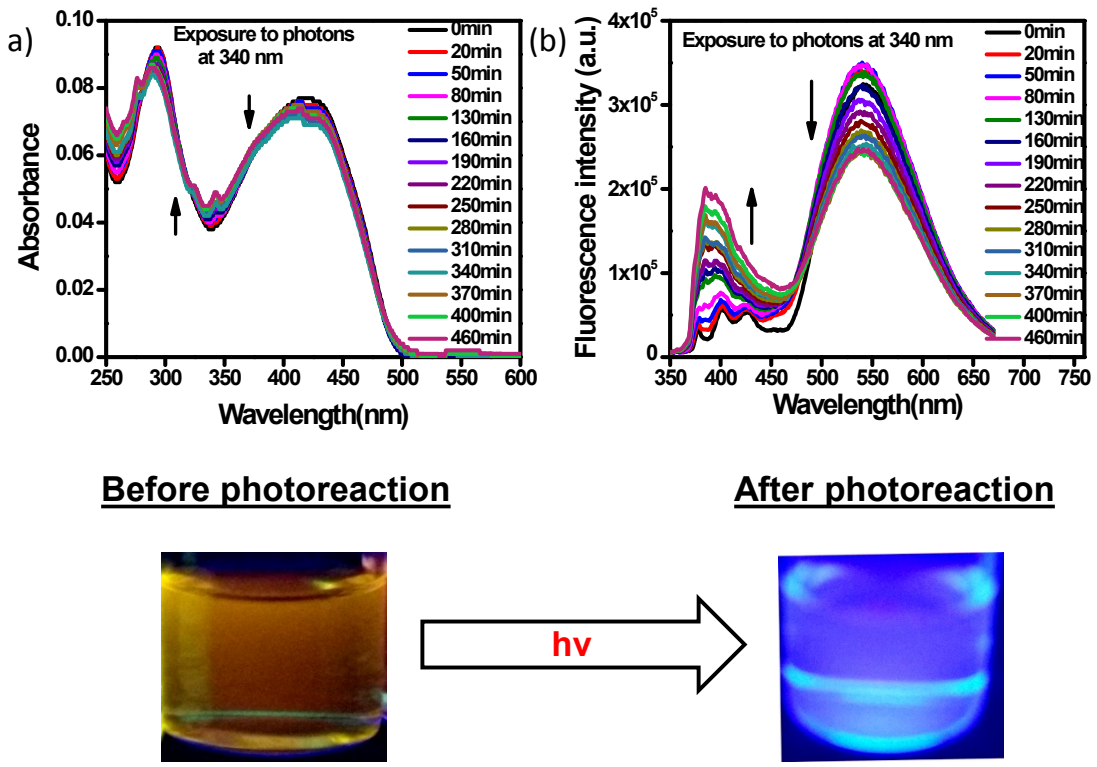


Figure S9. Steady-state (a) UV–visible absorption and (b) emission spectra of **PyEDY(PhNMe$_2$)$_2$** in isopropanol (c = 1 x 10^{-6} M, λ_{ex} = 340 nm) when irradiated at 340 nm for 460 minutes at the interval of 30 minutes in the presence of air. Photograph of **PyEDY(PhNMe$_2$)$_2$** in isopropanol under 365 nm UV lamp taken before and after photoreaction.

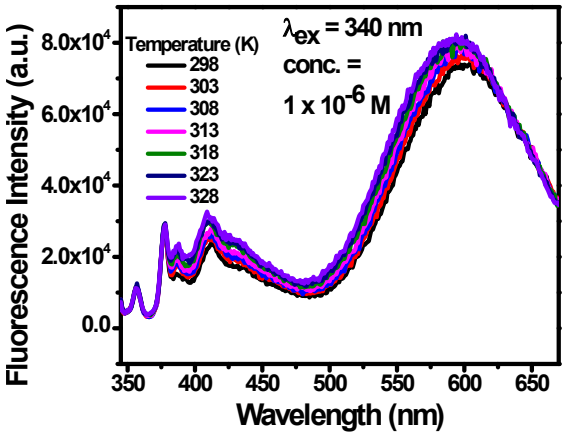


Figure S10. Steady-state emission spectra of **PyEDY(PhNMe$_2$)$_2$** in THF (c = 1 x 10^{-6} M, λ_{ex} = 340 nm) in the temperature range 25–55 ^{o}C in order to check cyclization in thermal conditions.

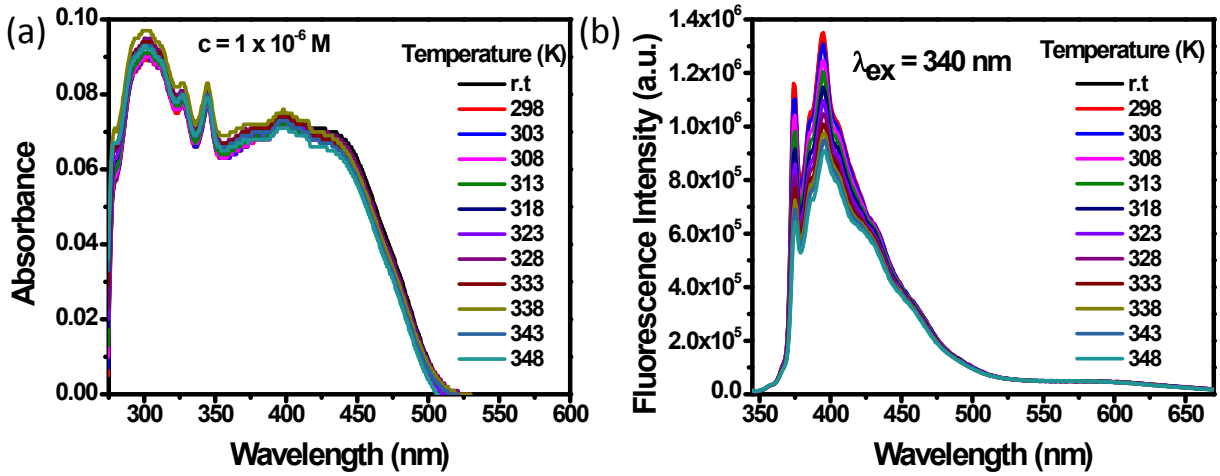


Figure S11. Steady-state (a) UV–visible absorption and (b) emission spectra of **PyEDY(PhNMe$_2$)$_2$** in DMF (c = 1 x 10^{-6} M, λ_{ex} = 340 nm) in the temperature range 25–75 ^{o}C in order to check the reversibility of cyclization in thermal conditions.

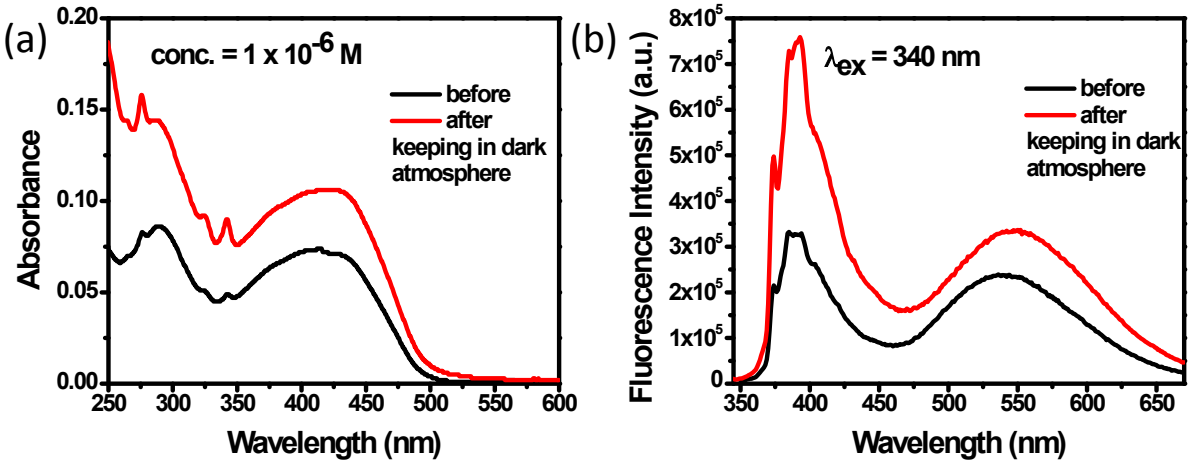


Figure S12. Steady-state (a) UV–visible absorption and (b) emission spectra of **PyEDY(PhNMe$_2$)$_2$** in isopropanol (c = 1 x 10^{-6} M, λ_{ex} = 340 nm) before and after keeping the sample in dark atmosphere for about a month in order to check the reversibility of cyclization.

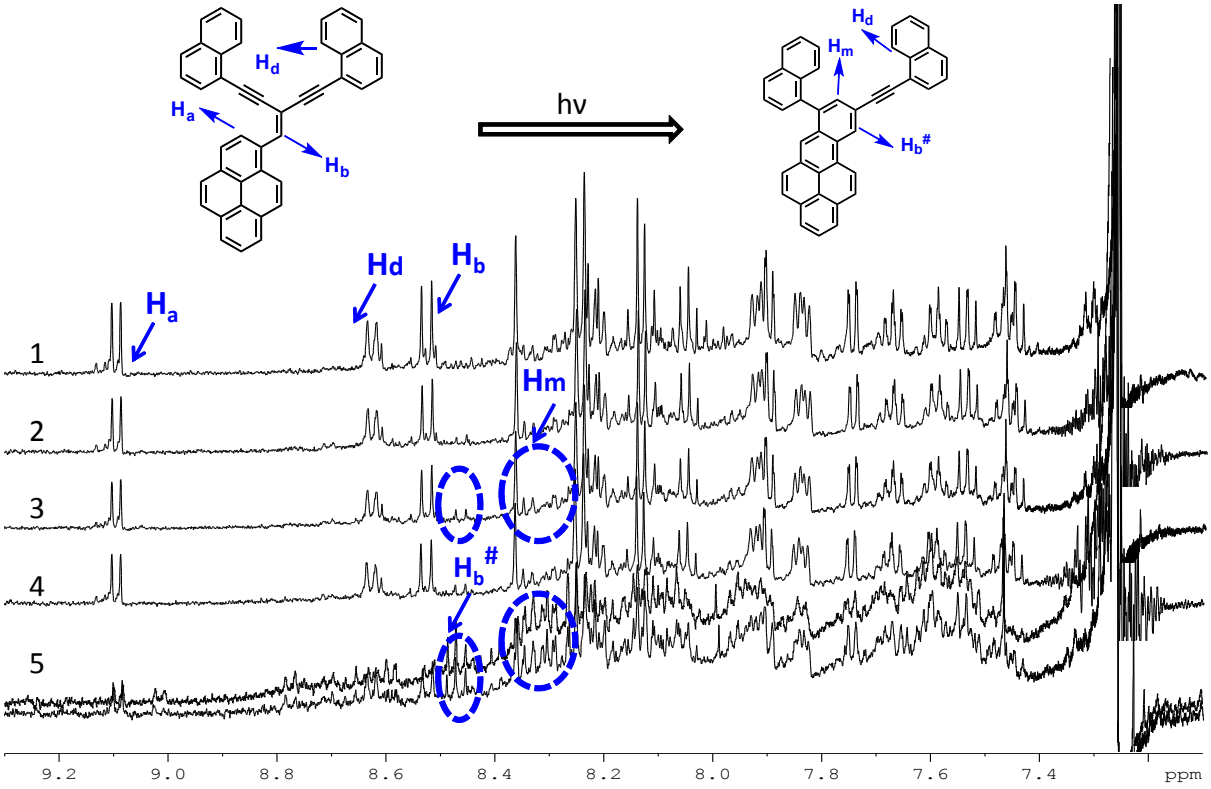


Figure S13. ^{1}H NMR spectrum of **PyEDYNap$_2$** in $CDCl_3$ (c = 1 x 10^{-3} M) upon irradiation under sunlight. Irradiation time is (1) 0 min; (2) 30 min; (3) 60 min; (4) 120 min; (5) 150 min.

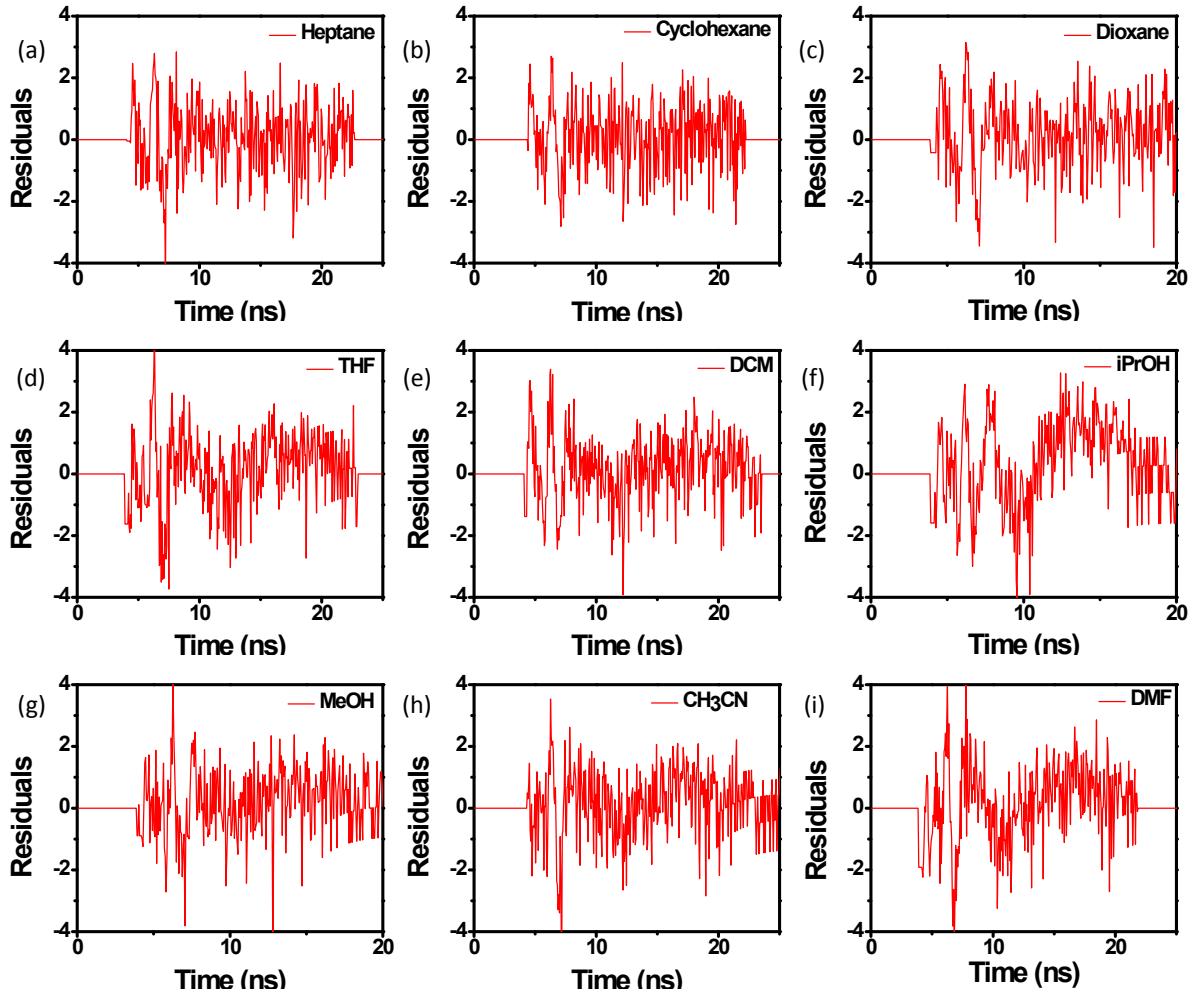


Figure S14. Residual plots for fluorescence decay profile of **PyEDY(PhNMe$_2$)$_2$** (λ_{em} = 500 nm) in different solvents (λ_{ex} = 450 nm, c = 1 x 10^{-6} M), a = heptane, b = cyclohexane, c = dioxane, d = THF, e = DCM, f = iPrOH, g = MeOH, h = CH_3CN and i = DMF.

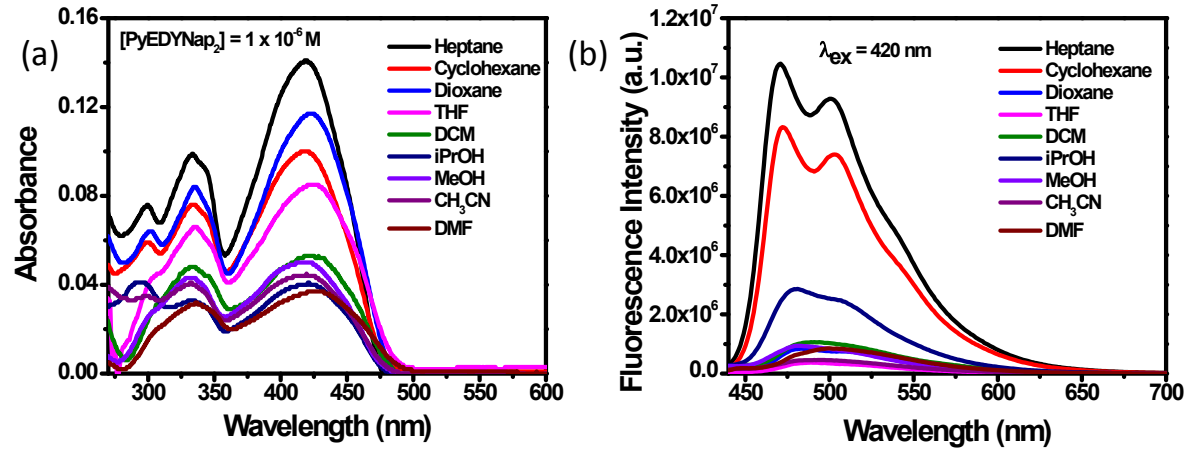


Figure S15. Steady-state (a) UV–visible absorption and (b) emission spectra of **PyEDYNap$_2$** in solvents of varying polarities (c = 1 x 10^{-6} M, λ_{ex} = 420 nm).

Cartesian co-ordinates of the optimized ground state geometry of the fluorophore (B3LYP/6-311g(d,p))

Optimized ground state geometry of PyEDY(PhNMe$_2$)$_2$ in cyclohexane

C	-6.46957	-1.48237	2.22873
C	-5.17149	-1.12337	2.57792
C	-4.08159	-1.51561	1.78648
C	-4.31560	-2.28976	0.61250
C	-5.65037	-2.66387	0.27012
C	-6.70917	-2.24487	1.09001
C	-2.72791	-1.18666	2.12459
C	-3.22029	-2.69550	-0.20977
C	-1.88590	-2.29740	0.11867
C	-1.68699	-1.55824	1.33419
C	-0.81376	-2.69766	-0.72335
C	-1.09184	-3.55944	-1.80081
C	-2.38080	-3.94526	-2.12122
C	-3.47107	-3.50994	-1.35312
C	-4.82098	-3.87257	-1.67165
C	-5.86368	-3.46417	-0.90151
H	-6.87992	-3.74517	-1.15734
H	-4.99403	-4.48641	-2.54948
H	-2.54411	-0.63294	3.03922
H	-7.30040	-1.16935	2.85126
H	-4.99020	-0.53541	3.47138
H	-7.72323	-2.52659	0.82682

H	-0.67815	-1.30492	1.62724
H	-0.26683	-3.89638	-2.41929
H	-2.55726	-4.58485	-2.97954
C	0.58720	-2.30797	-0.54183
H	1.31028	-3.10775	-0.67304
C	1.11890	-1.06069	-0.35495
C	2.53213	-0.90357	-0.23450
C	0.35799	0.14149	-0.32982
C	3.73054	-0.75301	-0.12848
C	-0.25559	1.18709	-0.33393
C	5.13357	-0.58522	0.00068
C	5.71023	0.69249	0.12538
C	6.00579	-1.68962	0.00591
C	7.07748	0.86141	0.25496
H	5.06627	1.56413	0.11665
C	7.37450	-1.53272	0.13439
H	5.59404	-2.68699	-0.09609
C	7.95555	-0.24916	0.27410
H	7.46720	1.86591	0.34144
H	7.99771	-2.41582	0.12580
C	-1.00185	2.39276	-0.33969
C	-0.37588	3.64604	-0.20779
C	-2.40192	2.38056	-0.48650
C	-1.10294	4.82336	-0.21799
H	0.70176	3.68845	-0.10068
C	-3.13822	3.55141	-0.49767
H	-2.91169	1.43089	-0.59620
C	-2.51224	4.81354	-0.35494
H	-0.57091	5.75917	-0.12041

H	-4.21002	3.48456	-0.61992
N	9.31543	-0.08833	0.42832
N	-3.24426	5.98132	-0.34470
C	10.20219	-1.23503	0.30761
H	10.16787	-1.68914	-0.69204
H	11.22461	-0.91538	0.50109
H	9.95287	-2.00852	1.04075
C	9.89468	1.24597	0.43601
H	9.47718	1.85537	1.24376
H	10.96733	1.16648	0.60355
H	9.73425	1.77951	-0.51080
C	-4.66929	5.94812	-0.63673
H	-5.20417	5.30876	0.07215
H	-5.07444	6.95419	-0.54334
H	-4.88187	5.58448	-1.65134
C	-2.56257	7.26650	-0.35182
H	-3.30448	8.06203	-0.30955
H	-1.91107	7.37474	0.52081
H	-1.95230	7.41374	-1.25339

Optimized ground state geometry of PyEDY($PhNMe_2$)$_2$ in acetonitrile

C	-6.52210	-1.44153	2.25477
C	-5.21671	-1.10620	2.60273
C	-4.13655	-1.50651	1.80133
C	-4.38743	-2.26439	0.61980
C	-5.72951	-2.61471	0.27918
C	-6.77863	-2.18802	1.10846
C	-2.77589	-1.20257	2.13777

C	-3.30198	-2.67872	-0.21190
C	-1.95970	-2.30438	0.11450
C	-1.74416	-1.58155	1.33776
C	-0.89767	-2.71441	-0.73633
C	-1.19331	-3.56306	-1.82031
C	-2.49011	-3.92516	-2.13905
C	-3.57044	-3.47852	-1.36218
C	-4.92764	-3.81725	-1.67909
C	-5.96084	-3.39981	-0.90008
H	-6.98219	-3.66206	-1.15444
H	-5.11385	-4.41964	-2.56182
H	-2.57994	-0.66480	3.05932
H	-7.34528	-1.12228	2.88385
H	-5.02304	-0.53138	3.50191
H	-7.79802	-2.45042	0.84691
H	-0.72999	-1.34945	1.63093
H	-0.37660	-3.91103	-2.44346
H	-2.68007	-4.55491	-3.00141
C	0.50992	-2.34845	-0.55586
H	1.21978	-3.15873	-0.69414
C	1.05952	-1.10954	-0.36223
C	2.47511	-0.96972	-0.24035
C	0.32150	0.10797	-0.33593
C	3.67589	-0.82736	-0.13567
C	-0.25325	1.17691	-0.34591
C	5.08057	-0.67233	-0.01098
C	5.66944	0.60124	0.11944
C	5.94331	-1.78649	-0.01178
C	7.03798	0.75802	0.24368

H	5.03459	1.47988	0.12283
C	7.31329	-1.64307	0.11129
H	5.52314	-2.78079	-0.11121
C	7.90899	-0.36216	0.24463
H	7.43703	1.75788	0.34066
H	7.92851	-2.53171	0.10419
C	-0.93446	2.42023	-0.35874
C	-0.24411	3.63353	-0.16465
C	-2.32614	2.49359	-0.56943
C	-0.89924	4.85100	-0.18146
H	0.82688	3.61190	0.00120
C	-2.99283	3.70484	-0.58822
H	-2.88728	1.57897	-0.72152
C	-2.29994	4.92839	-0.39634
H	-0.32163	5.75141	-0.02745
H	-4.06079	3.70477	-0.75449
N	9.26549	-0.21393	0.36932
N	-2.95402	6.13161	-0.41888
C	10.13676	-1.38163	0.36155
H	10.05759	-1.94150	-0.57735
H	11.16818	-1.05530	0.47330
H	9.90655	-2.06543	1.18644
C	9.85191	1.11302	0.50326
H	9.48362	1.63092	1.39605
H	10.93160	1.01626	0.59163
H	9.63795	1.74220	-0.36833
C	-4.39381	6.18334	-0.63765
H	-4.94289	5.64417	0.14264
H	-4.71793	7.22141	-0.62094

H	-4.67250	5.75646	-1.60778
C	-2.21714	7.37350	-0.22425
H	-2.90920	8.21005	-0.28709
H	-1.73109	7.40878	0.75743
H	-1.44690	7.51235	-0.99133

Reference

1) A. Singh, A. K. Pati, and A. K. Mishra, *Phys. Chem. Chem. Phys.,* 2018, **20**, 4167–4180.