Electronic Supplementary Information

Engineering Molecular Self-Assembly of Perylene Diimide Through pH-responsive Chiroptical Switching†

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Contents

Experimental section

Materials and methods

Materials. 3,4,9,10-Perylenetetracarboxylic dianhydride (PDA), L-histidine and imidazole were obtained from Sigma-Aldrich. All other reagents and solvents utilized in the experiments were of reagent and spectroscopic grades and used as received without further purification unless otherwise mentioned. Milli-Q water was used in all the experiments.

Absorption Spectroscopy. UV–vis absorption spectra of **HPH** (50 μM solution in Milli-Q water) were recorded on a Perkin Elmer Model Lambda 900 spectrophotometer by using quartz cuvette of 10 mm path length.

Fluorescence emission Spectroscopy. Fluorescence emission spectra of **HPH** (50 μM solution in Milli-Q water) were recorded on a Perkin Elmer Model LS 55 spectrophotometer by using quartz cuvette of 10 mm path length. All fluorescence spectra were recorded with excitation wavelength of λ_{ex} = 480 nm.

Circular Dichroism (CD). CD measurements of **HPH** (50 μM solution in Milli-Q water) were carried out on a Jasco J-815 spectropolarimeter under nitrogen atmosphere by using quartz cuvette of 10 mm path length. Isodesmic model fitting was crried out by reported method.[1] The obtained temperature versus CD intensity (mdeg) at 572 nm data is normalized between 0 and 1 using the below mentioned formula.

$$\alpha(T) = \theta_T-\theta_M/\theta_{agg}-\theta_M$$

Where, $\alpha(T)$ is the fraction of aggregation, θ_T is the CD effect (mdeg) at a given temperature T, θ_M is the CD effect (mdeg) at high temperature corresponding to the monomer, θ_{agg} is the CD effect (mdeg) at low temperatures corresponding to the aggregated state.
The fraction of aggregation ($\alpha(T)$) versus temperature curve was fitted to the isodesmic model using the Boltzman equation.

$$y = A2 + (A1-A2)/(1 + \exp((x-x_0)/dx))$$

Where A1 = minimum value of the $\alpha(T)$

A2 = maximum value of the $\alpha(T)$

x_0 = melting temperature (*T*m at $\alpha(T)= 0.5$)

dx = characteristic temperature that is related to the slope of the function at the melting temperature.

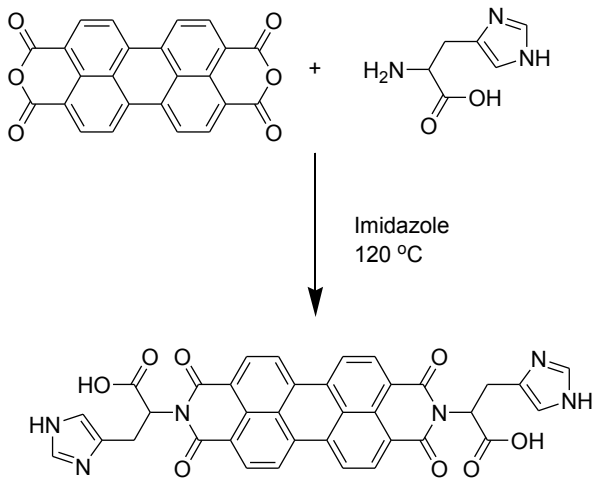
The average stack length of the aggregates (DP_N) was calculated using equations

$$DPN= 1/(1-\alpha(T))^{1/2}$$

NMR Spectroscopy. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer with chemical shifts reported as ppm (in DMSO-d_6 with tetramethylsilane as internal standard).

Mass Spectrometry (MS). High resolution mass spectra (HRMS) were obtained from Agilent Technologies 6538 UHD Accurate-Mass Q-TOF LC/MS spectrometer.

Field Emission Scanning Electron Microscopy (FESEM). FESEM images were acquired with a FEI Nova nanoSEM-600 equipped with a field-emission gun operating at 15 kV. The samples were prepared by drop casting of respective solutions onto a Si (111) substrate and dried in air followed by vacuum drying at room temperature.



HPH

Synthetic procedure and characterisation of HPH[2]

3,4,9,10-Perylenetetracarboxylic dianhydride (PDA) (500 mg, 1.2 mmol), L-histidine (435 mg, 2.5 mmol), and imidazole (2.0 g) were added into a round bottom flask fallowed by heating at 120 ºC for 1 h under vigorous stirring and nitrogen atmosphere. The reaction mixture was allowed to cool to 90 ºC, transferred into Milli-Q water and filtered. The filtrate was acidified with 2.0 N HCl, and the precipitate was filtered, washed with excess of methanol, Milli-Q water, acetone and dried under vacuum at 42 ºC to obtain the product **HPH** in good yield (76%). ^{1}H NMR (*DMSO-d*$_6$, 400 MHz) δ_H 14.01 (2H, br), 8.92 (2H, d), 8.64 (4H, s), 8.40 (4H, br), 7.43 (2H, s), 5.86 (2H, q), 3.71 (2H, dd), 3.46 (2H, dd); ^{13}C NMR (*DMSO-d*$_6$, 100 MHz) δ_C 169.6, 162.1, 134.0, 133.7, 131.2, 129.7, 128.2, 123.8, 121.7, 119.1, 116.8, 52.6, 23.8; Elemental analysis: Found C, 64.88; H, 3.35; N, 12.60; calcd C, 64.86; H, 3.33; N, 12.61 for $C_{36}H_{22}N_6O_8$; HR-MS: m/z found 667.1567 $[M+H]^+$; calcd. 666.1499 for $C_{36}H_{22}N_6O_8$.

pH responsive UV-vis absorption spectra of **HPH**

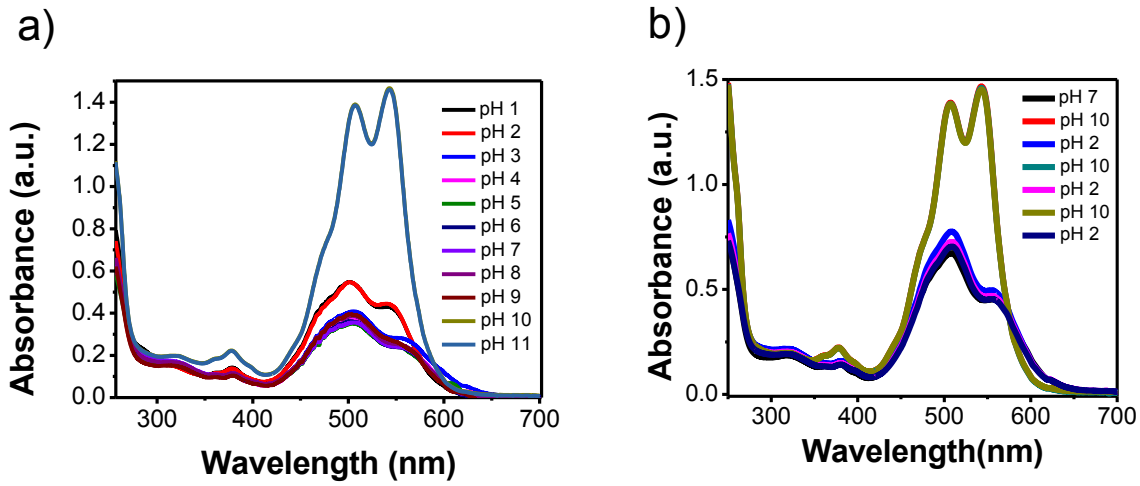


Figure S1. a) pH dependent UV-vis absorption spectra of **HPH**. b) pH responsive reversible absorption switching spectra of **HPH**.

pH responsive fluorescence emission spectra of **HPH**

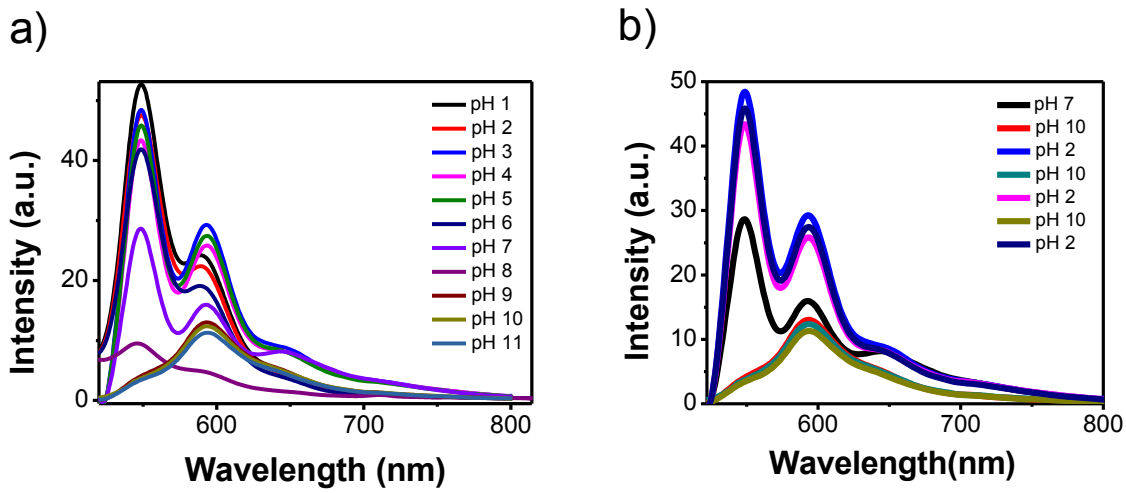


Figure S2. a) pH dependent Fluorescence emission spectra of **HPH**. b) pH responsive reversible emission switching spectra of **HPH**.

pH responsive CD spectra of **HPH**

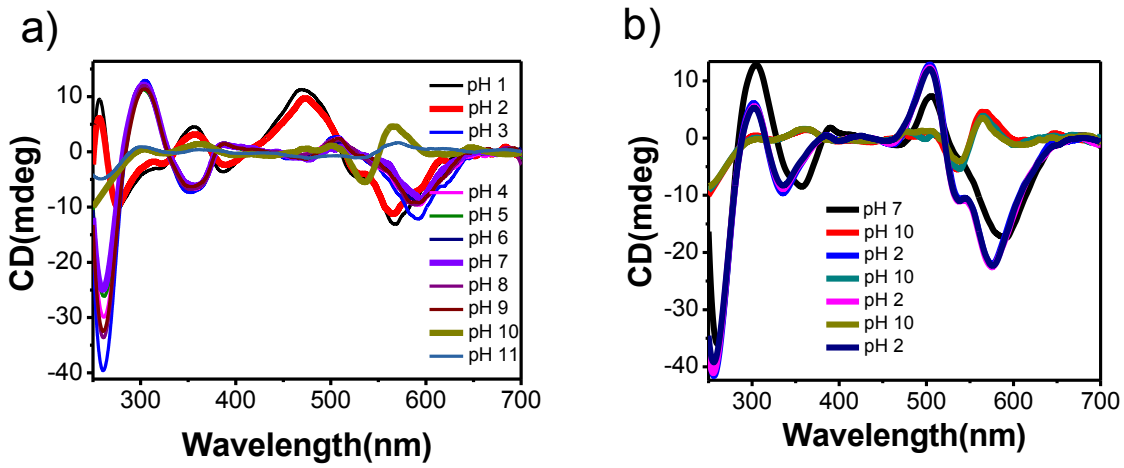


Figure S3. a) pH dependent CD spectra of **HPH**. b) pH responsive reversible chirootical switching spectra of **HPH**.

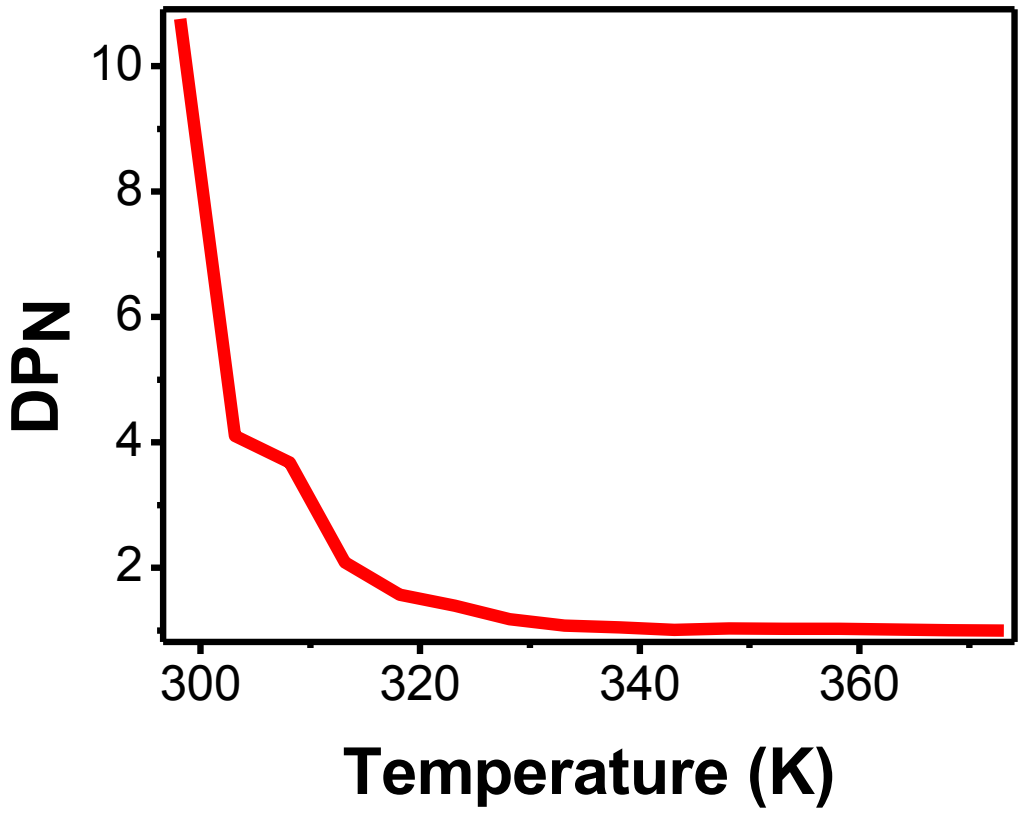
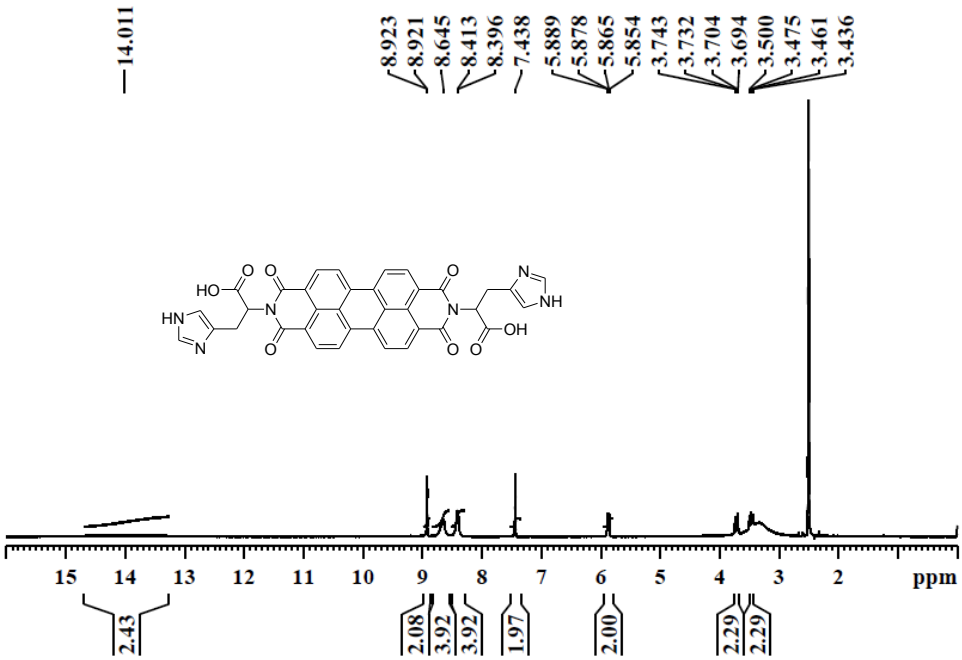
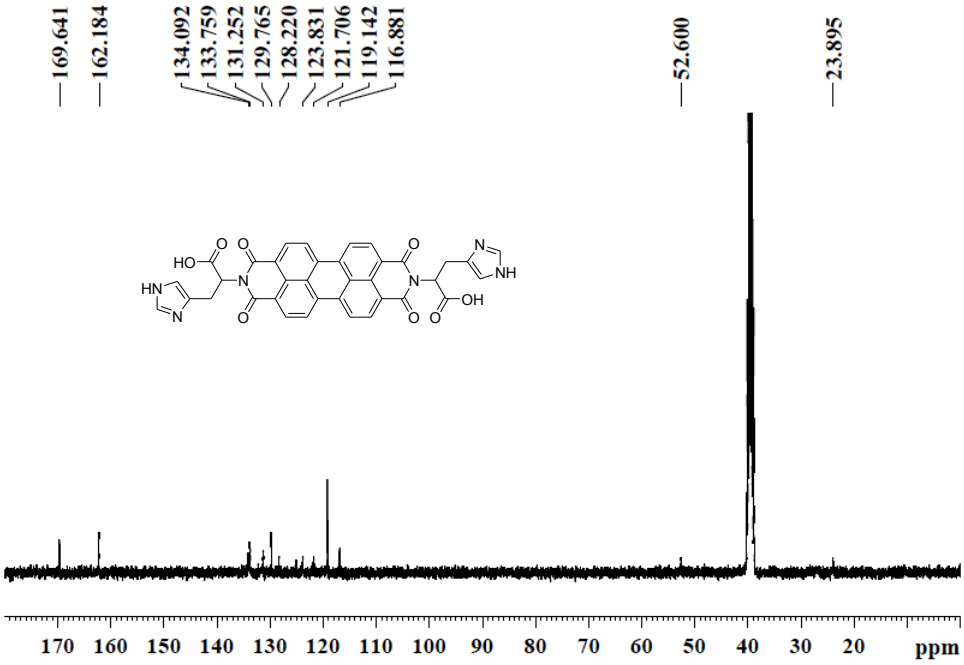


Figure S4. The Plot of average stack length (DP_N) for **HPH** in water as a function of temperature.

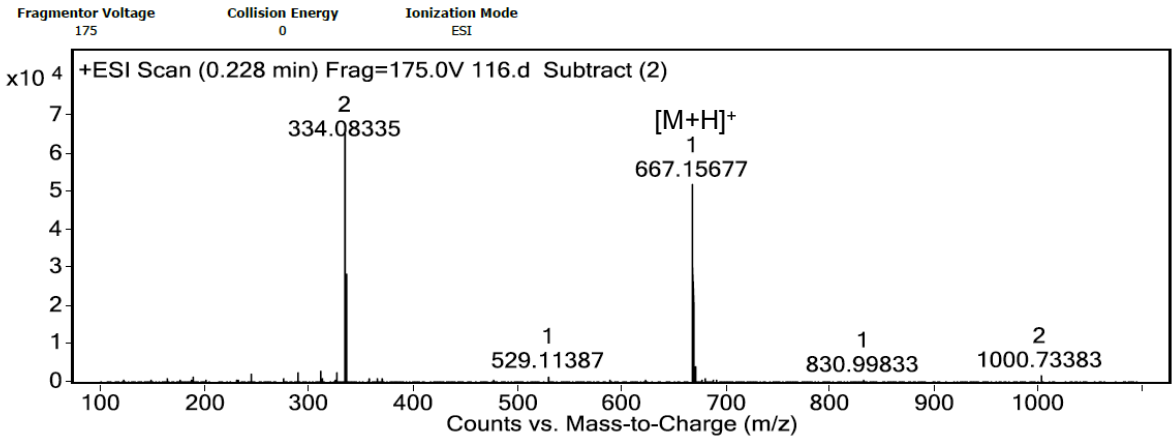
^{1}H NMR spectra (DMSO-*d6*, 400 MHz) of **HPH**



^{13}C NMR spectra (DMSO-*d6*, 100 MHz) of **HPH**



HRMS of **HPH**



References

1. (a) N. Ponnuswamy, G. D. Pantos, M. M. Smulders and J. K. Sanders, *J. Am. Chem. Soc.*, 2012, **134**, 566-573; (b) M. M. J. Smulders, M. M. L. Nieuwenhuizen, T. F. A. de Greef, P. van der Schoot, A. P. H. J. Schenning and E. W. Meijer, *Chem. - Eur. J.*, 2010, **16**, 362-367.
2. A. K. Dwivedi, M. Pandeeswar and T. Govindaraju, *ACS Appl. Mater. Interfaces*, 2014, **6**, 21369-21379.