Supporting Information

Fluorescent Coronene Monoimide Gels via H-bonding Induced Frustrated Dipolar Assembly

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Experimental Procedures

General. Unless otherwise noted, all reagents were used as received and all reactions were carried out under an argon atmosphere. ^{1}H NMR and ^{13}C NMR were recorded on Bruker AVANCE-400 MHz spectrometer at room temperature.

Field Emission Scanning Electron Microscopy (FE-SEM). FE-SEM measurements were performed on NOVA NANO SEM 600 (FEI) operated at 15 kV, by drop casting the solution on glass substrate. Some of the samples were recorded with gold sputtering and some of them recorded in low vacuum mode (FE-SEM).

Atomic Force Microscopy (AFM). AFM measurements were performed on Veeco diInnova SPM operating in tapping mode regime. Micro-fabricated silicon cantilever tips doped with phosphorus with frequency 1 Hz and spring constant 0.9 Nm^{-1} were used. The samples were prepared by drop casting solutions on glass substrate.

Optical Measurements. Electronic absorption spectra were recorded on Perkin Elmer Lambda 900 UV-Vis-NIR Spectrometer. UV-Vis spectra were recorded in 3 mm and 1 mm path length quartz cuvettes.

Confocal Microscopy Imaging: Confocal Microscopy imaging was done at room temperature using a Zeiss LSM 510 META laser scanning confocal microscope. The microscope objective of 63X (NA 1.4) and 20X (NA 0.5) were employed. Sample was prepared by sealing the solution between two glass plates.

Circular Dichroism Measurements: Circular dichroism (CD) measurements were carried out on a Jasco J-810 spectropolarimeter.

Theoretical Optimization: The monomer and the dimer of CMI were optimized using Gaussian-03 suite of programs.[1] The optimization was carried out within Density Functional Theory (DFT) using B3LYP[2,3] hybrid exchange-correlation functional and 6-31G basis set. The optimized geometries were visualized using Visual Molecular Dynamics (VMD).[4]

1. Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.
2. A. D. Becke, *J. Chem. Phys.*, **1993**, *98*, 5648.
3. C. Lee, W. Yang and R.G. Parr, *Phys. Rev. B*, **1988**, *37*, 785.
4. W. Humphrey, A. Dalke, K. Schulten, *J. Molec. Graphics*, **1996**, *14*, 33.

Foot Note Details for the main text:

UV-vis spectra of CMI-CH at 90 °C is much broader compared to the one in gel state at 25 °C even though the chromophores are in disjunction with each other in the latter resembling a molecularly dissolved chromophore situation. This can be probably because of doppler and collisional deactivations. Ideally when there is no electronic coupling between the molecules the bandwidths decrease with decreasing temperature. We believe that at temperatures less than 30 °C where the chromophores start to decouple from each other such deactivation mechanisms gain preference over the usually predominant π-π electronic coupling induced broadening.

Experimental Section

Coronene-1,2-dicarboxylic anhydride has been synthesized according to the reference: B. Yang, Y. Li, M. G. Xie, *Chinese Chemical Letters*, **2003**, *14*, 783-785.

General Procedure for imidation:

Coronene-1,2-dicarboxylic anhydride (0.296 mmol), trialkoxy substituted gallic amide amine derivative (a) (0.538 mmol), imidazole (5 g) and zinc acetate (100 mg) were thoroughly mixed and heated with stirring to reflux (150 °C) for 8 hours. Then the reaction mixture was transferred under hot conditions in to 1M HCl and subsequently it was extracted with chloroform. The organic layer was repeatedly washed with 1M HCl. Then the organic layer was washed with saturated NaCl solution, dried using anhydrous Na_2SO_4 and then filtered. After evaporating the solvent under reduced pressure the crude product, which was reddish orange in colour was purified by column chromatography (silica gel, started with 100% chloroform to 2 % methanol in chloroform) and Bio-beads (S-X3) size exclusion column chromatography.

Coronene monoimide-chiral (**CMI-CH**): ^{1}H NMR ($CDCl_3$): 9.18 (d, 2H), 8.72 (m, 4H), 8.54 (d, 2H), 8.41 (d, 2H), 7.36 (t, 1H), 7.21 (s, 2H), 4.29 (d, 2H), 4.06 (m, 8H), 1.9 (m, 6H), 1.20-1.50 (m, 24H), 0.85 (m, 27H) ppm. MALDI-TOF/MS *m/z* (%): 985.61 $[M]^+$, 1007.667 $[M+Na]^+$, 1023.637 $[M+K]^+$ calculated for $C_{65}H_{80}N_2O_6$, 985.37 gmol^{-1}.

Coronene monoimide-achiral (**CMI-ACH**): ^{1}H NMR ($CDCl_3$):): 9.35 (d, 2H), 8.88 (m, 4H), 8.65 (d, 2H), 8.57 (d, 2H), 7.34 (t, 1H), 7.17 (s, 2H), 4.30 (d, 2H), 4.07 (t, 2H), 3.98 (m, 6H), 1.88 (m, 6H), 1.19-1.26 (m, 54H), 0.87 (m, 9H) ppm. MALDI-TOF/MS *m/z* (%): 1109 $[M+K]^+$ calculated for $C_{71}H_{92}N_2O_6$, 1069.53 gmol^{-1}.

Supporting Figures

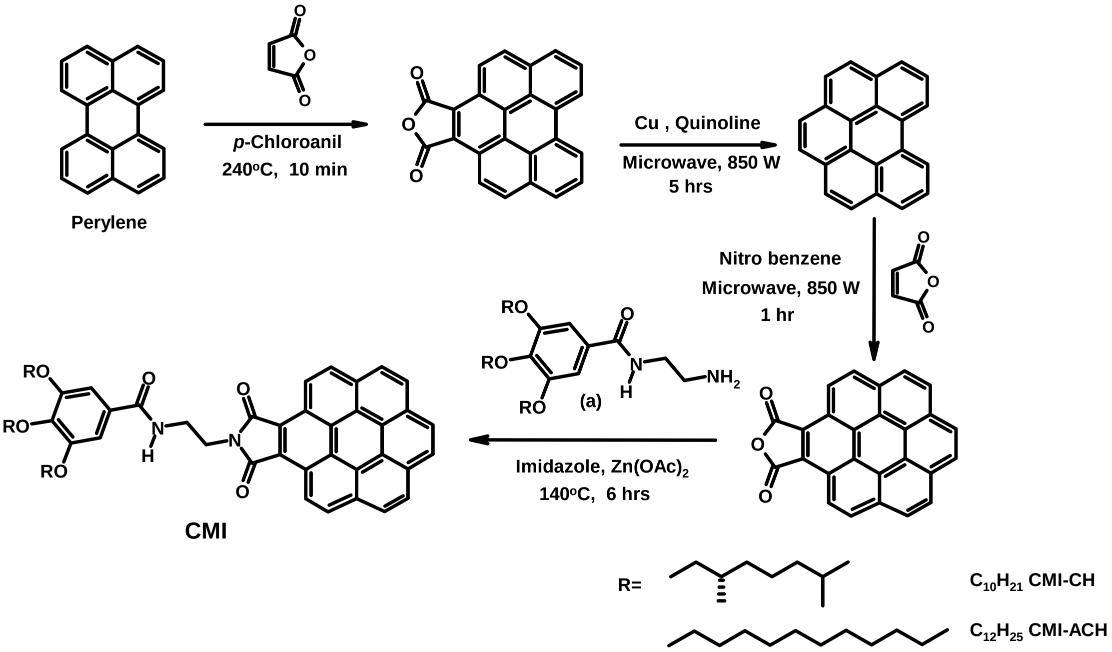

Fig. S1. Synthetic route to coronene monoimides, **CMI-CH** and **CMI-ACH.**

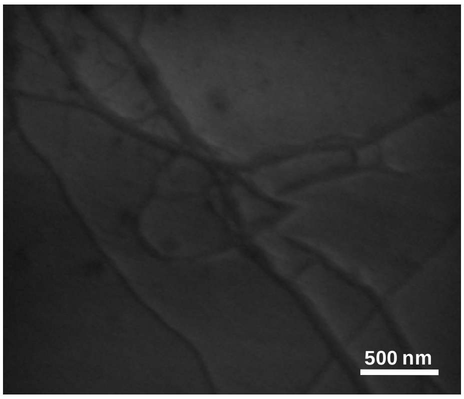

Fig. S2: FE-SEM image of **CMI-CH** gel (2 mM) in toluene drop-casted on a glass substrate.

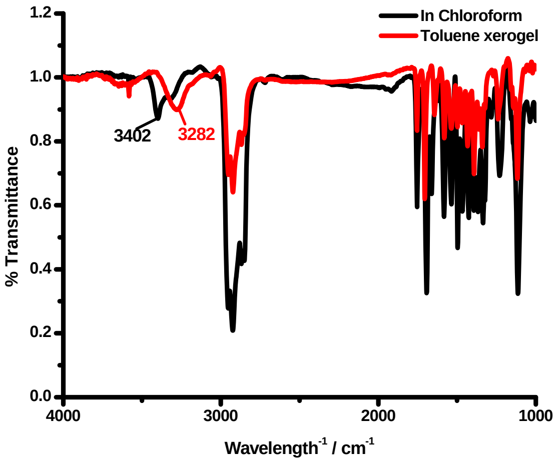

Fig. S3 FT-IR spectra of **CMI-CH** in film state evaporated from a solution of different solvents.

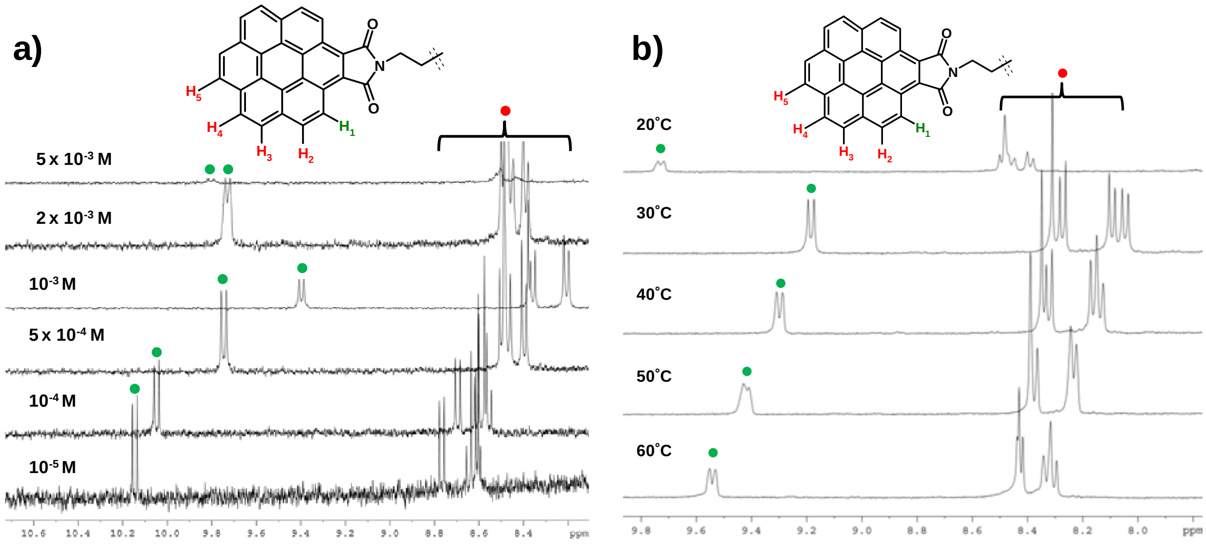

Fig. S4 a) and b) Concentration (25 °C) and temperature (2 mM) dependent ^{1}H-NMR of **CMI-CH**, respectively in toluene-d8.

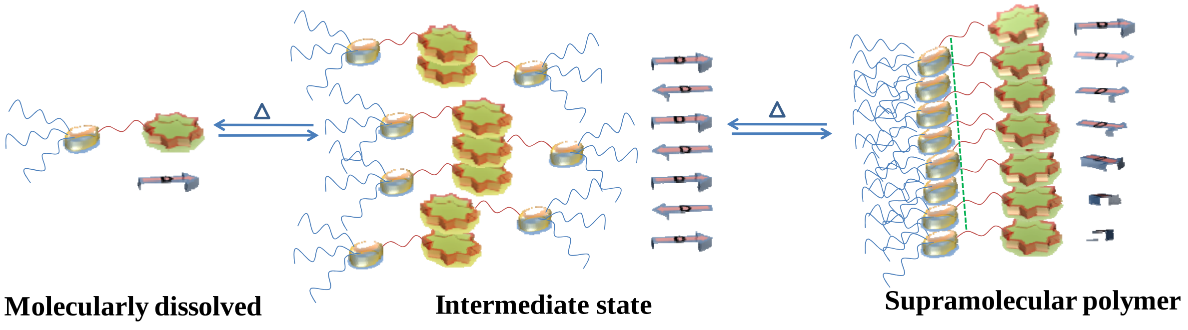

Fig. S5 Proposed two stage self-assembly process in **CMI-CH**.

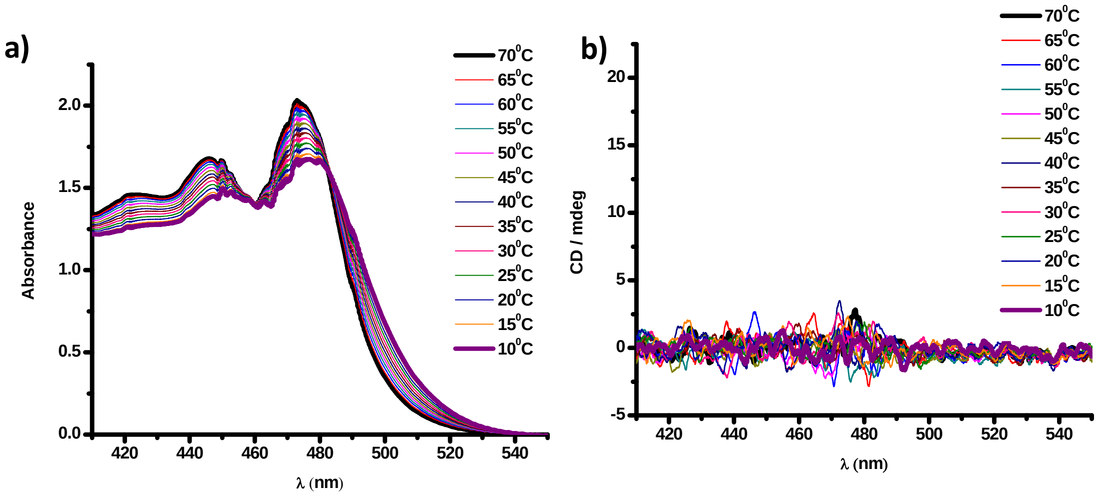

Fig. S6 Temperature dependent a) absorption spectra and b) CD spectra of **CMI-CH** (2 mM, toluene) + 1 μl of TFA.

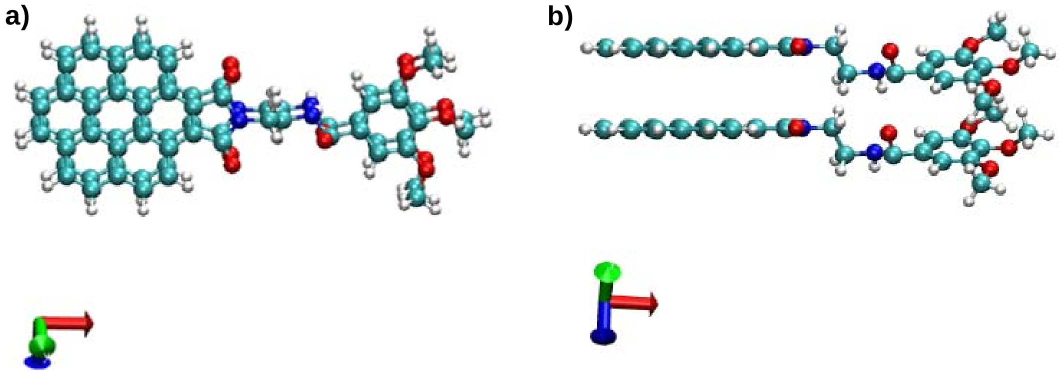

Fig. S7 Initial conformation of the energy minimized CMI derivatives.