Electronic Supplementary Material (ESI) for Soft Matter.
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Supporting Information

Co-assembly of Donor and Acceptor towards Organogels Tuned by Charge Transfer Interaction Strength

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Experimental details

Compounds

All starting materials were obtained from commercial suppliers and were used as received. All solvents were distilled with suitable drying agents.

The synthesis of acceptor NDI. Naphthalenetetracarboxylic-1,8:4,5-bisanhydride (2.5 g, 9.3 mmol) and imidazole (20 g) was put into a 2-neck flask. The flask was evacuated and refilled with nitrogen several times. Then 6-undecyl amine (3.19 g, 18.6 mmol), was injected into the reaction mixture. The reaction mixture was heated to 130 °C for 4 h. After cooling down to room temperature, the mixture was poured into water and precipitate was filtered. The crude product was washed with water and methyl alcohol, then dried under vacuum to yield the white product **NDI** (4.8 g, 90%). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K): δ= 8.73 (s, 4H), 5.21-5.11 (m, 2H), 2.26-2.15 (m, 4H), 1.89-1.78 (m, 4H), 1.18-1.34 (m, 24H), 0.80-0.84 (t, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K): δ = 126.9, 77.4, 77.0, 76.5, 32.2, 31.6, 26.4, 22.5, 14.0. MS (MALDI-TOF): m/z (M^+) = 573.5 (calcd for $C_{36}H_{50}N_2O_4$: 574.4).

Gel formation

Gels were formed by dissolving the gelators in hot chloroform to make a clear solution. Then the solution was cooled down to room temperature, and the organogels formed. Gelation was determined by the absence of flow of the solvent when the tube was inverted. To measure the critical gelation concentration, we increased the solvent chloroform by 50 μL every time to the compound mixtures (NDI&PyC0, NDI&PyC3, NDI&PyC0, and NDI&PyC3) until the concentration was insu□cient to form a stable gel. All gels were aged for at least 12 h before being subjected to further characterizations.

Characterizations

UV/Vis spectra and FL spectra were recorded in a quartz cuvette or on a quartz slide by using a Hitachi UV-4100 spectrophotometer and a HORIBA–JOBIN YVON FluoroMax-4 spectrofluorometer, respectively. Samples for FTIR, AFM and SEM were cast onto freshly cleaved mica surfaces and then dried in vacuum for at least 48 hours at RT. FTIR spectra were performed by using a Bruker HQL005 FTIR spectrometer (Thermo Electron Corporation) by using the Transmission method (TR). AFM images were recorded on a Bruker Multimode 8 Microscopy. SEM measurements were carried on a FEI Quanta FEG 250 instrument. Samples for XRD characterization were cast onto cleaned silicon wafer (100) surfaces and the solvent was first evaporated naturally in air and then dried in vacuum overnight. XRD studies were performed by using Rigaku max-ra X-ray diffractometer. Samples for TEM were dropped on copper grids covered with carbon film and the solvent was evaporated naturally overnight. TEM measurements were conducted on a FEI TECNAI 20. CD spectra were measured in quartz cuvettes by using a JASCO J-815 spectrophotometer.

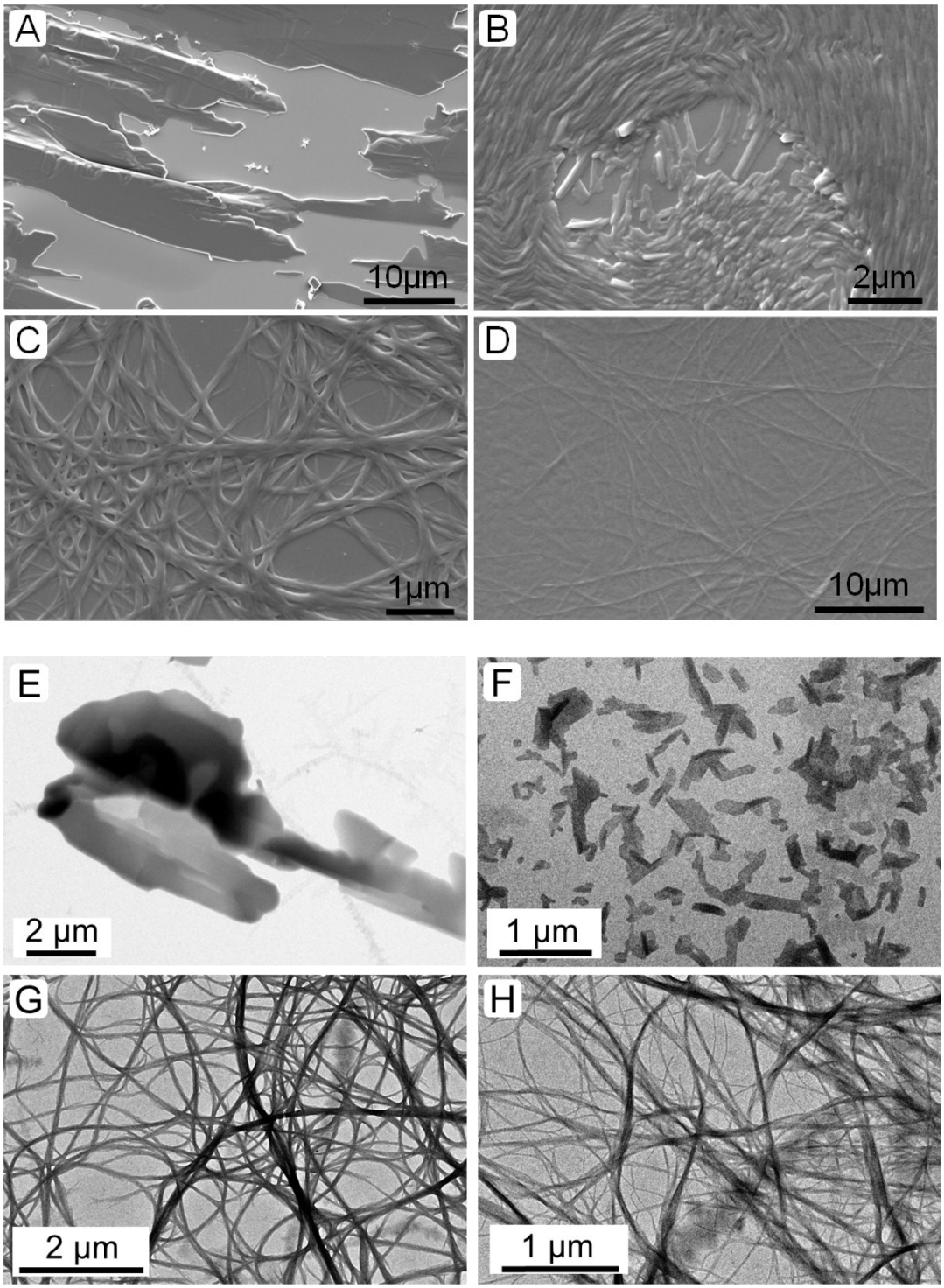

Fig S1. SEM (A-D) and TEM (E-H) images of single component samples in chloroform. A, E) NDI. B, F) PDI. C, G) PyC0. D, H) PyC3. The concentration of NDI is 2.4 mg mL^{-1}, PDI is 2.8 mg mL^{-1}, and PyC is 7 mg mL^{-1}.

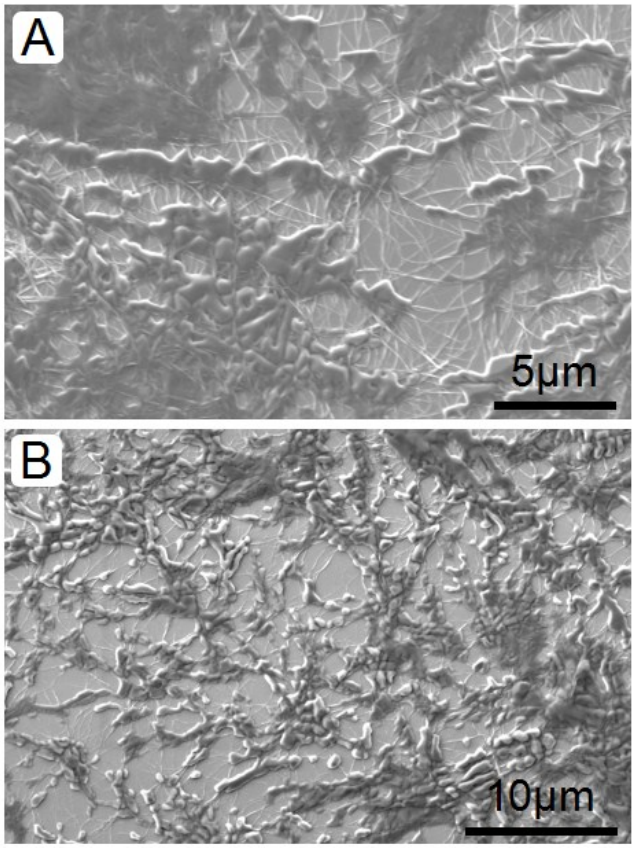

Fig S2. SEM images of donor-acceptor (1:1) gels. A) NDI&PyC0. B) NDI&PyC3. The concentration of PyC0 is 7 mg mL^{-1}, and PyC3 is 13 mg mL^{-1}.

The nanostructures from acceptor NDI in the 1:1 D-A gel mixtures seem to be smaller than that from only NDI molecules, it would be due to the disturbance of the donor fiber structures.

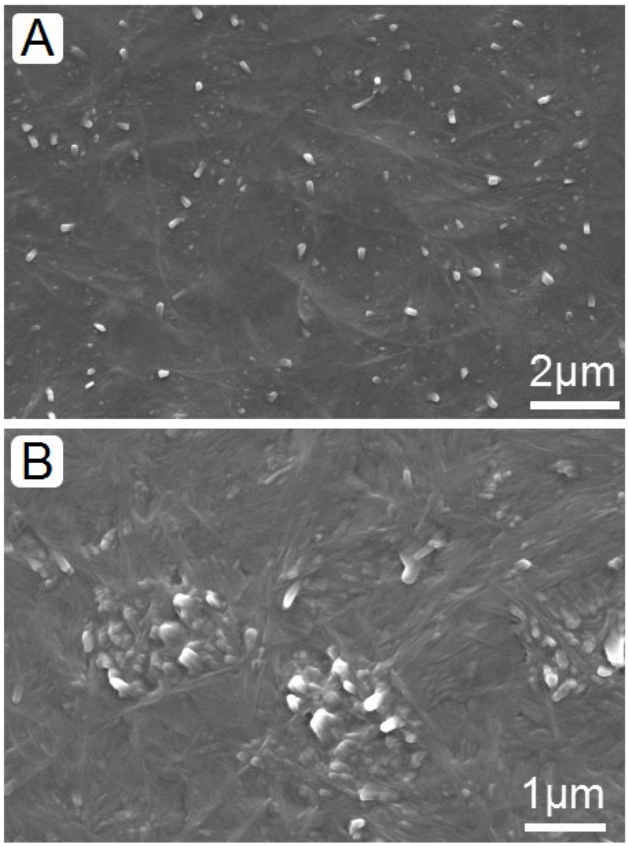

Fig S3. SEM images of donor-acceptor (1:1) gels. A) PDI&PyC0. B) PDI&PyC3. The concentration of PyC0 is 8 mg mL^{-1}, and PyC3 is 13 mg mL^{-1}.

The nanostructures from acceptor PDI in the 1:1 D-A gel mixtures seem to be shorter than that from only PDI molecules, because they were embedded in the fiber networks and only the ends of the sticks could be observed.

Table S1. The critical gel concentration (CGC) of donor-acceptor gels with different molar ratios.

composition	state	CGC[a] (mg/mL)	
		1:1[b]	1:2[c]
NDI&PyC0	Gel	13	9
NDI&PyC3	Gel	7	7
PDI&PyC0	Gel	13	5
PDI&PyC3	Gel	8	5

a) the concentration is for the donors. b) the molar ratio is 1: 1 (donor : acceptor). c) the molar ratio is 2:1 (donor : acceptor).

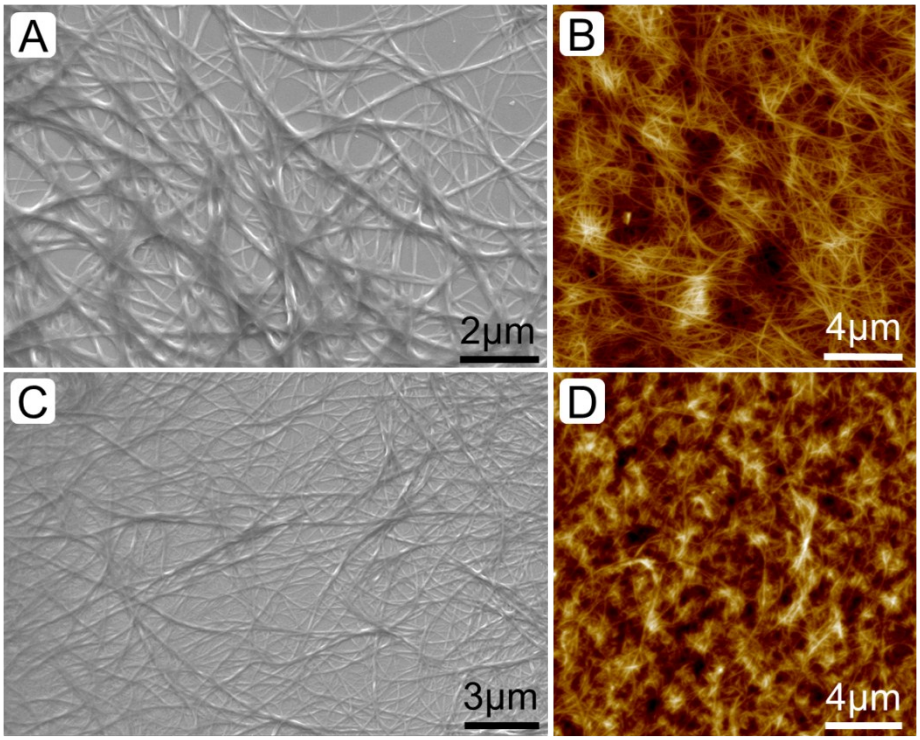

Fig S4. SEM (A, C) and AFM (B, D) images of donor-acceptor (2:1) gels. A, B) NDI&PyC0. C, D) NDI&PyC3, and the concentration of PyC in all gels is 10 mg mL^{-1}.

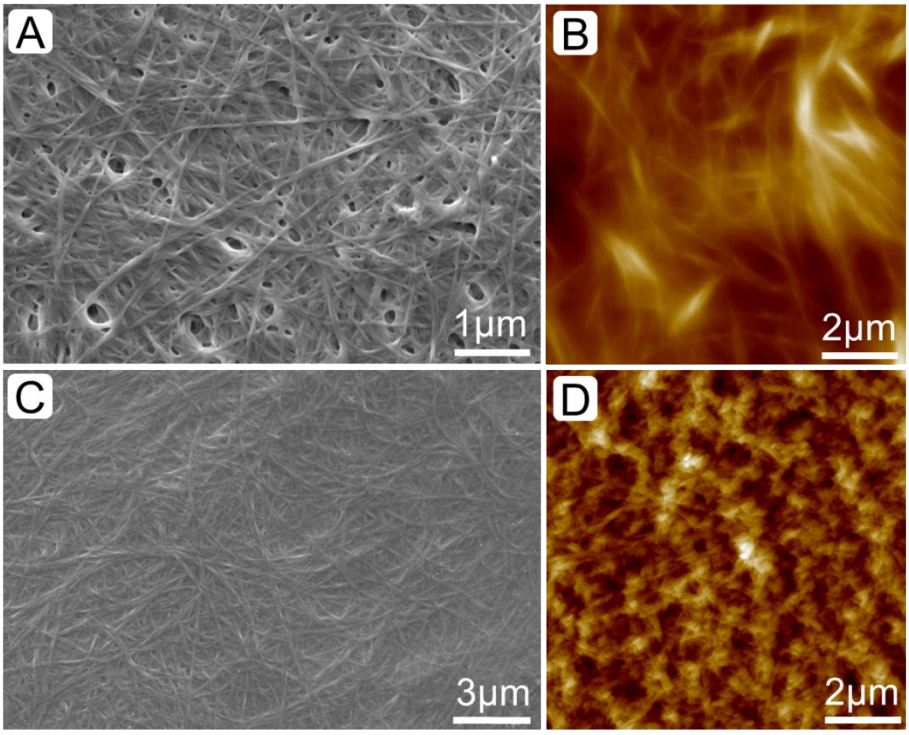

Fig S5. SEM (A, C) and AFM (B, D) images of donor-acceptor (2:1) gels. A, B) PDI&PyC0. C, D) PDI&PyC3. And the concentration of PyC in all gels is 10 mg mL^{-1}.

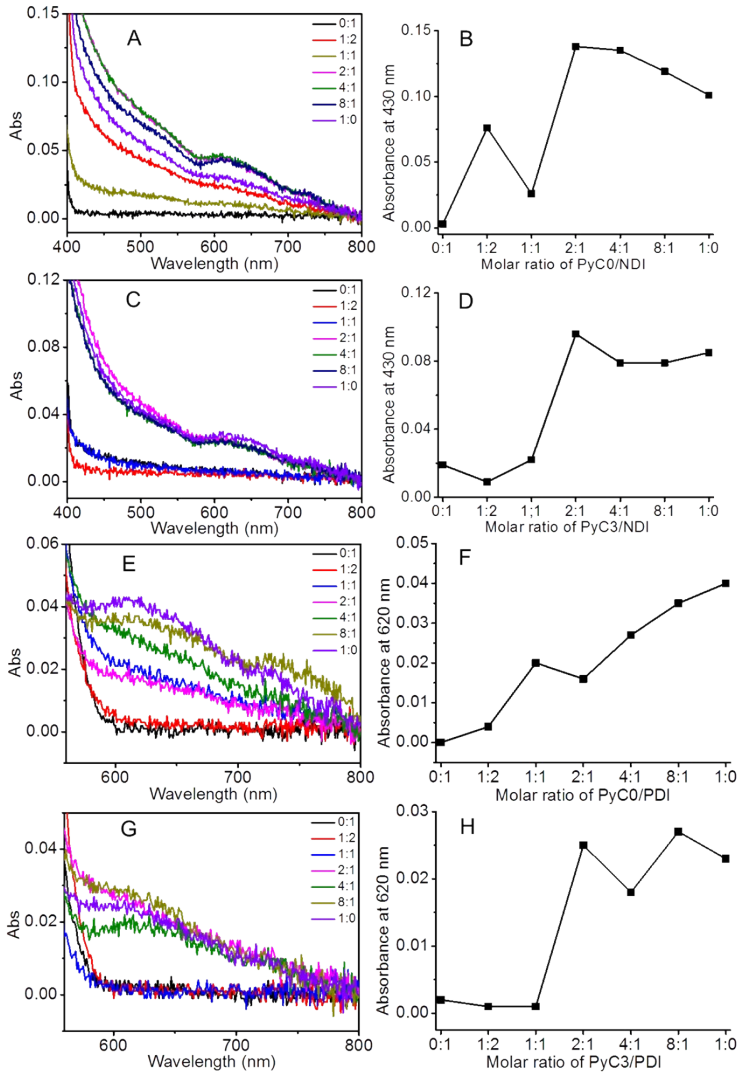

Fig S6. UV-vis spectra (A, C, E, G) in chloroform for the titration of donor and acceptor at longer wavelength to show the CT-band clearly. And Job's plots (B, D, F, H) by probing the charge-transfer absorbance at a certain wavelength for corresponding co-assembly. A, B) NDI&PyC0, c = 8mM. C, D) NDI&PyC3, c = 6mM. E, F) PDI&PyC0, c = 5mM. G, H) PDI&PyC3, c = 4mM. The optical path length for all the measurements is 0.1 mm.

For cogel of PyC0&NDI, scattering due to the aggregates of complexes of PyC0&NDI exists, for example the absorption at the molar ratio of 1:2 (PyC0:NDI). However, this scattering absorption diminishes with increasing the ratio of PyC0. For cogel of PyC3&NDI, the absorption from the scattering due to the aggregated NDI also diminishes with increasing the ratio of PyC3. The CT complexes composed of NDI shows the maximum absorption at 430 nm with the molar ratio of 2:1 (PyC:NDI), which is the same ratio to that used for our investigation in the manuscript. For cogels of PyC3&PDI, new CT absorption band at about 620 nm could be clearly observed. No obvious maximum absorption for the CT band could be obtained, although the cogels with molar ratio of PyC:PDI larger than 1:1 (PyC0:PDI) or 2:1 (PyC3:PDI) show elevated absorption.

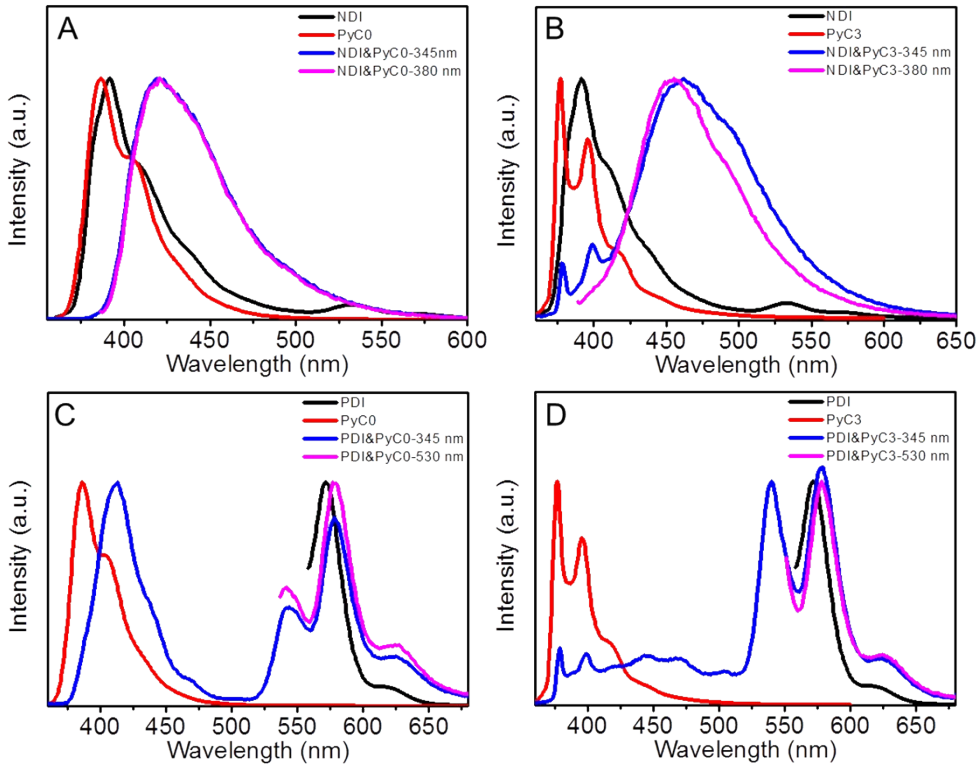

Fig. S7. Normalized FL spectra of diluted solutions NDI, PDI, PyC and the CT gels in chloroform. (A) NDI, PyC0, and NDI&PyC0 gel. (B) NDI, PyC3, and NDI&PyC3 gel. (C) PDI, PyC0, and PDI&PyC0 gel. (D) PDI, PyC3, and PDI&PyC3 gel. The excitation wavelength: solution NDI - 380 nm; solution PDI - 530 nm; solution PyC0 - 345 nm; solution PyC3 - 345 nm; gel NDI&PyC0 – 345 and 380 nm; gel NDI&PyC3 - 345 and 380 nm; gel PDI&PyC0 – 345 and 530 nm; PDI&PyC3 - 345 and 530 nm. The concentration of NDI and PDI is 0.0125 mg mL^{-1}. The concentration of solution PyC0 and PyC3 is 0.025 mg mL^{-1}. A molar ratio of 2:1 (donor to acceptor) was used, and the concentration of donors were kept at 10 mg mL^{-1}.

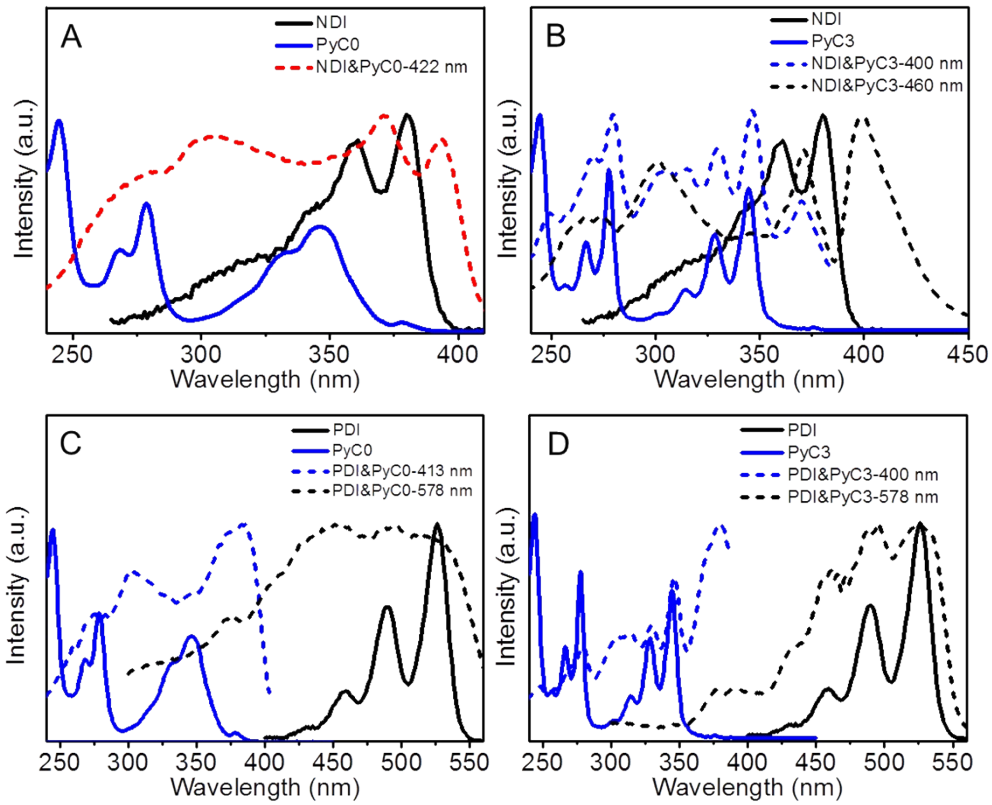

Fig. S8. Normalized absorption spectra of diluted solutions NDI, PDI, PyC (solid lines) and excitation spectra (short dash lines) of the donor-acceptor (2:1) cogels. (A) NDI, PyC0, and NDI&PyC0 gel. (B) NDI, PyC3, and NDI&PyC3 gel. (C) PDI, PyC0, and PDI&PyC0 gel. (D) PDI, PyC3, and PDI&PyC3 gel. The excitation spectra of the cogels were collected at: NDI&PyC0 - 422 nm; NDI&PyC3 - 400 and 460 nm; PDI&PyC0 – 413 and 578 nm; PDI&PyC3 - 400 and 578 nm. The concentration of NDI and PDI is 0.0125 mg mL^{-1}. The concentration of solution PyC0 and PyC3 is 0.025 mg mL^{-1}. A molar ratio of 2:1 (donor to acceptor) was used for the cogels, and the concentration of donors were kept at 10 mg mL^{-1}.

From Fig. 8, it can be seen that all excitation spectra are red shifted compared to the monomeric absorption of corresponding donors or acceptors, indicating the emission were all from the assembled donors or acceptors instead of CT complexes.

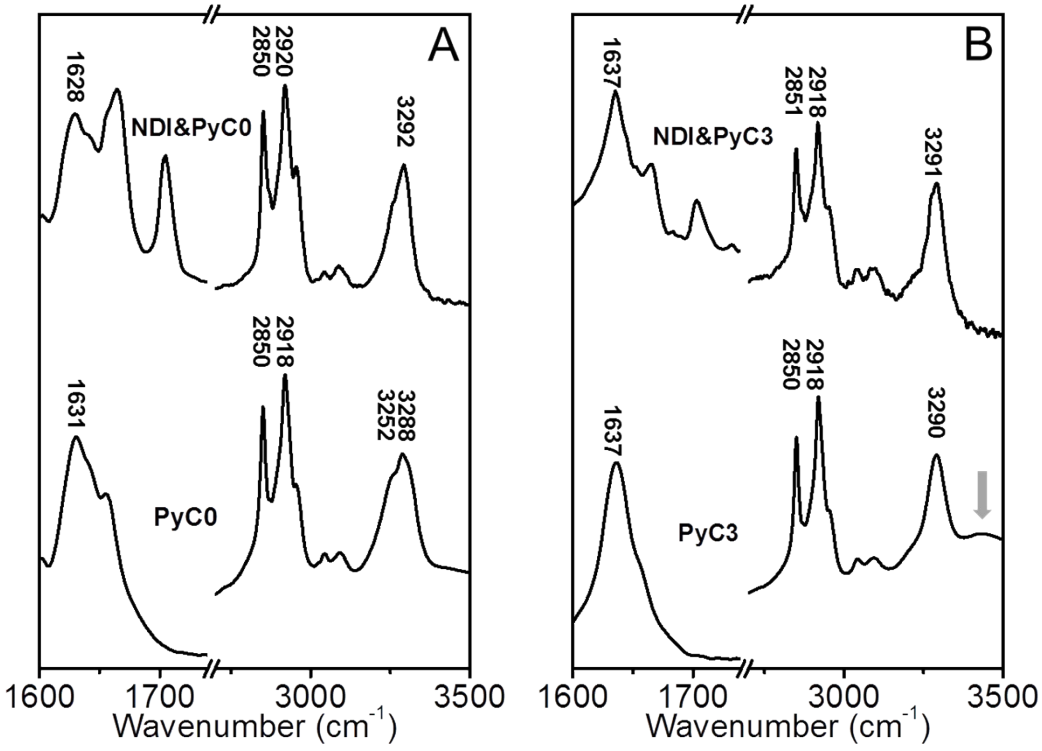

Fig. S9. FT-IR spectra of powder PyC0 and PyC3 and the CT gels formed in chloroform. A) PyC0 and NDI&PyC0 gel. B) PyC3 and NDI&PyC3 gel.

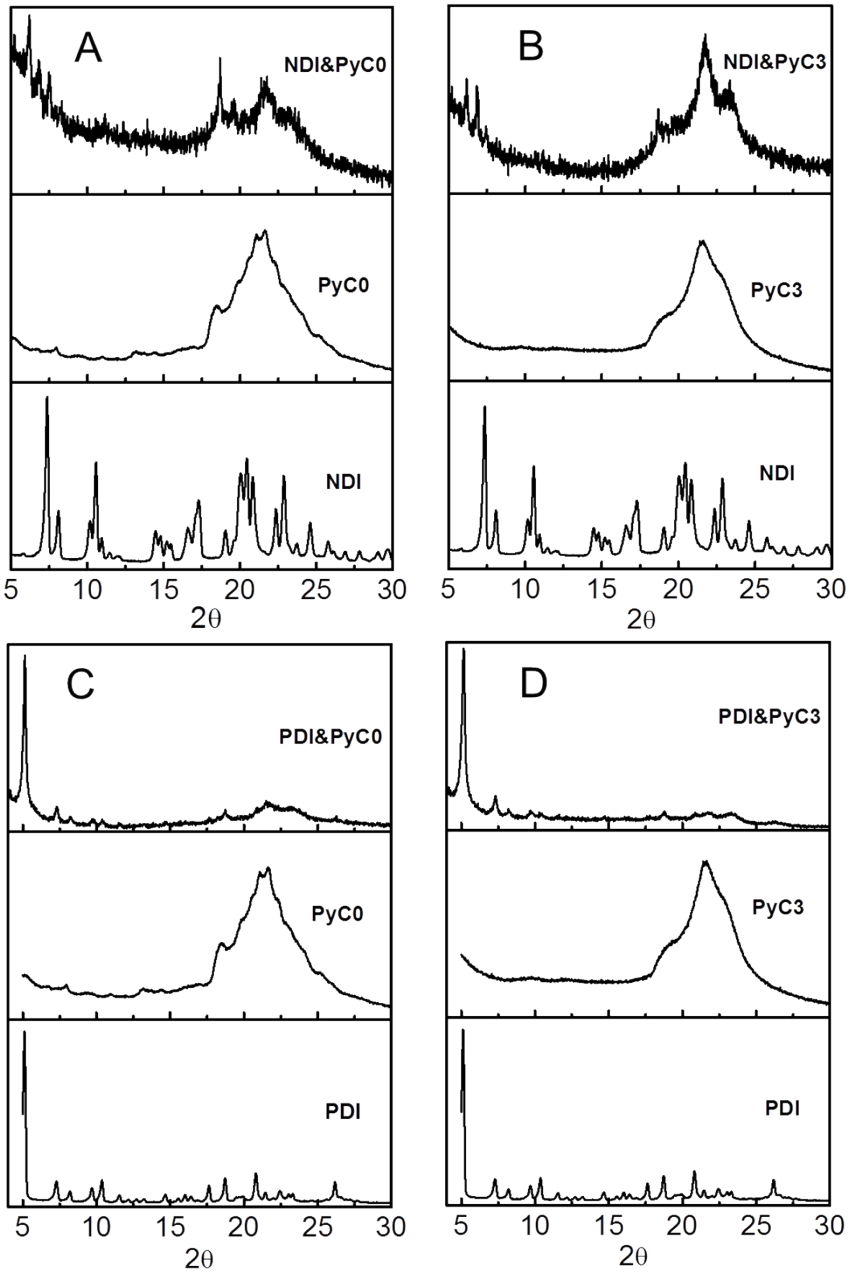

Fig. S10. XRD spectra of NDI, PDI, PyC0, PyC3 powder and the CT gels formed in chloroform. A) NDI, PyC0, and NDI&PyC0 gel. B) NDI, PyC3, and NDI&PyC3 gel. C) PDI, PyC0, and PDI&PyC0 gel. D) PDI, PyC3, and PDI&PyC3 gel. The ratio of donor to acceptor is 2 to 1, and the concentration of PyC0, PyC3 in all gels is 10 mg mL^{-1}.

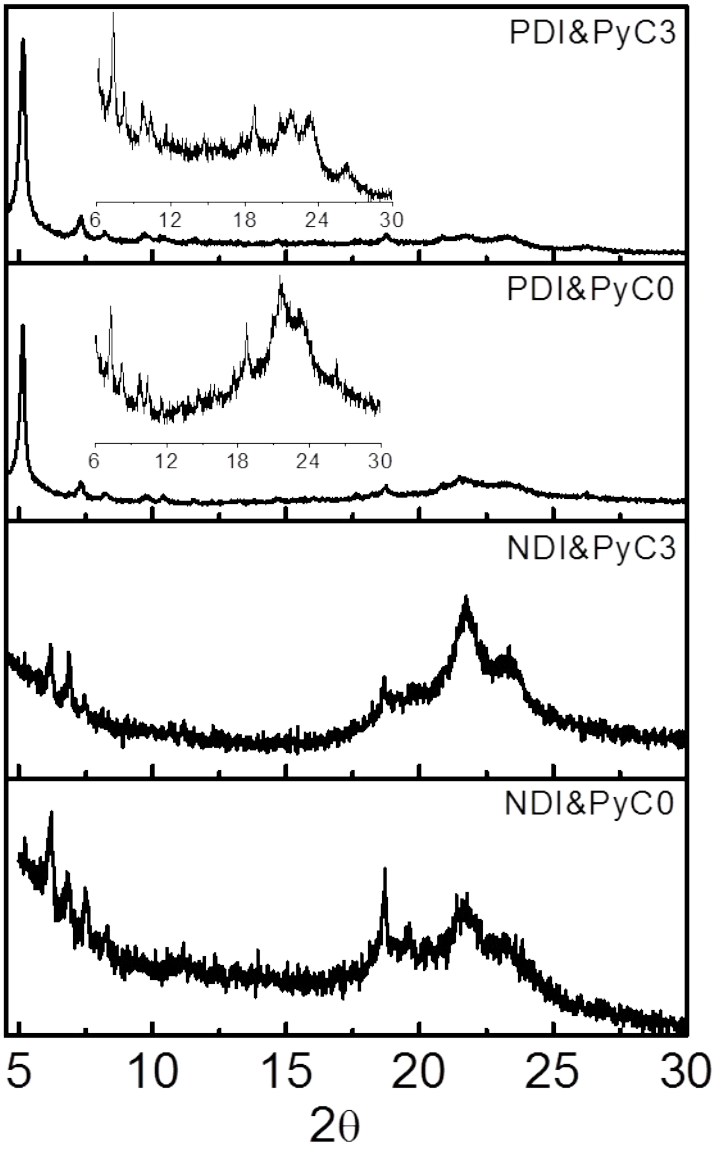

Fig. S11. XRD spectra of the CT gels formed in chloroform. The ratio of donor to acceptor is 2 to 1, and the concentration of PyC in all gels is 10 mg mL^{-1}.

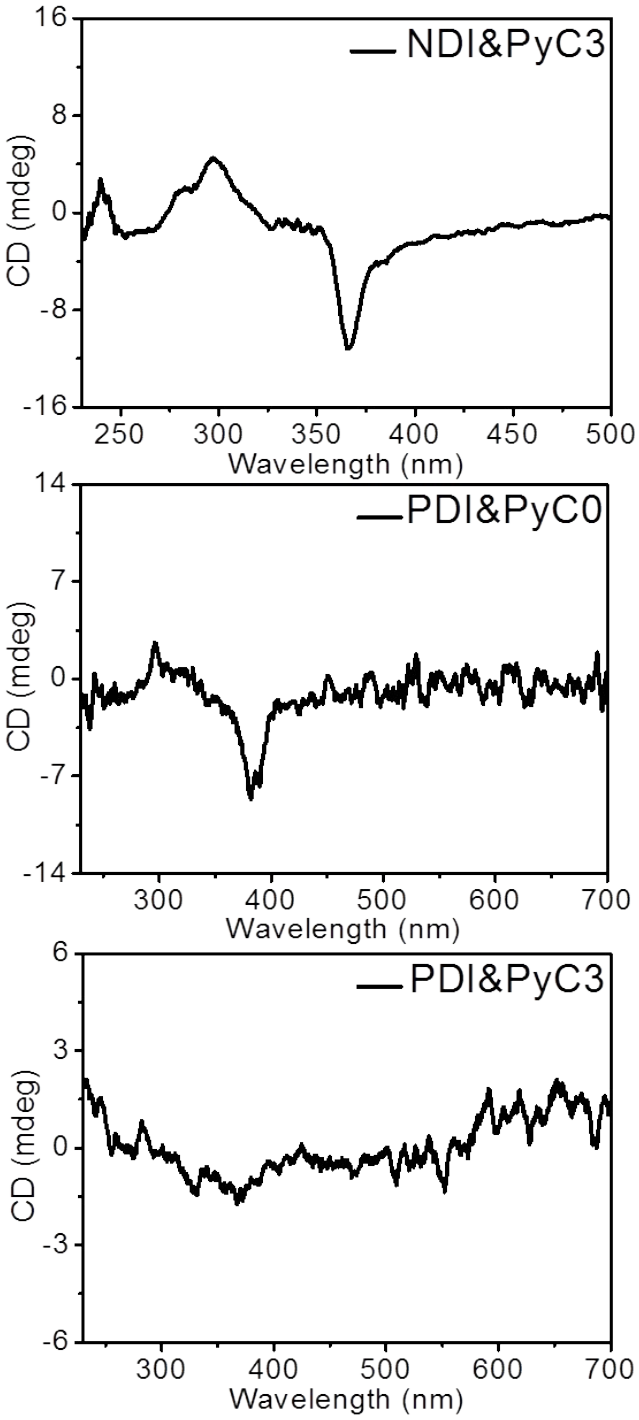

Fig S12. CD spectra of CT gels in chloroform. The ratio of donor to acceptor is 2 to 1, and the concentration of PyC in all gels is 10 mg mL^{-1}.