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Supplementary Information

Crystallization-Induced Red Emission of a Facilely Synthesized Biodegradable Indigo Derivative

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Experimental Section

Indigo and other reagents were purchased from Aldrich and used without further purification.

Synthesis of Indigoid-B[1]

Typically, a mixture of indigo (1.05 g, 4 mmol) and 4-dimethylaminopydine (DMAP, 0.76g, 6 mmol) were dissolved in 200 mL of CH_2Cl_2. Di-*tert*-butyldicarbonate ((t-Boc)$_2$O, 3.3g, 15mmol) was added dropwise in the solution with ice bath for cooling, followed by stirring at room temperature for 24 h. The reaction mixture was washed with water to remove excess (t-Boc)$_2$O and BOC-DMAP complexes and further dried over anhydrous $MgSO_4$. The crud product was obtained after removing solvent by reducing pressure. It was recrystallized from EtOAc, yielding (80%) red crystalline product. ^1H NMR (300 MHz, $CDCl_3$), δ (ppm):1.64 (s, 18H), 7.21(m, 2H), 7.61(m, 2H), 7.75(d, 2H), 8.01(d, 2H).

Synthesis of Indigoid-A[2]

Based on a modified Blanc's method, indigo (1.0 g, 4.35 mmol) and pyridine (5 mL) were dispersed in 100 mL ethyl acetate under stirring. Under the protection of nitrogen atmosphere, acetyl chloride (5 mL) was added dropwise into the solution. Then the reaction mixture was heated to 100 ℃ and reacted for 24 h. The reaction mixture was washed with water for three times and the organic phase was obtained. After concentration, the product was obtained via purification by silica column chromatography using dichloromethane/hexane=9/1 as elution solvent, yielding (18%) red powder. ^1H NMR (300 MHz, $CDCl_3$), δ (ppm):2.58 (s, 6H), 7.28(m, 2H), 7.71(m, 2H), 7.80(d, 2H), 8.31(d, 2H).

Preparation of Indigoid aggregates (microcrystals) dispersion in THF/water with different ratios

Indigoid-B or Indigoid-A (100 μL of 0.01 M CH_2Cl_2 solution) was dissolved in different amounts of THF (x mL), followed by the slow addition (22.5 mL/h by syringe pump) of a known volume of water ((10-x) mL) with or without treatment in an ultrasonic cleaner (SB-120 DTN, power: 120 W) bath. Through this typical process, we obtain a series of Indigoid-B and Indigoid-A dispersion with different water contents (f_w = 0%, 10%, 20%, 30%, 40%, 50%, 60 %, 70 %, 80%, 90%, 95%).

Instruments and Characterization

The samples were dissolved with chloroform-d for ^{1}H NMR measurements on a Bruker AV300 MHz NMR spectrometer. Emission spectra of indigoids solutions were measured by fluorescence spectrophotometry on an PerkinElmer LS-55 at 25 ℃ (stimulation slit width: 5 nm, emission slit width: 5 nm, scanning speed: 120 nm/min^{-1}). UV/Vis spectra of the samples in THF/water solutions were measured on a SHIMADZU UV-2450 spectrophotometer. After drop-casting on the silicon substrate and air-drying for 24h at room temperature, the samples were gold sputtering treated. The morphologies of microcrystals were measured by field emission scanning electron microscopy (FESEM, JEOL, JSM6701F) and fluorescence microscopy (OLYMPUS IX71). The relative FL intensity shown in Figure 1&3 in the paper is obtained by calculation based on the integration area ratio of emission band. Transmission electron microscopy (TEM, JEOL JEM-2100F) operating at 200kV was used to further confirm the detailed morphologies in solutions. The XRD patterns were obtained by Bruker 6000 X-ray diffractometer using a Cu K α source.

Total energies of different torsional conformers of Indigoid-A and Indigoid-B were computed using the Perdew-Burke-Ernzerhof functional (DFT–PBE)[3], as implemented in the Vienna Ab initio Simulation Package (VASP)[4, 5]. The calculations were performed using a plane-wave basis with a cut-off kinetic energy of 450 eV. Electron–ion interactions were described by the projector-augmented wave (PAW) method[6,7]. Indigoid-B and Indigoid-A was modeled in a unit cell of 20 x 20 x 20 Å, and the Brillouin zone was sampled by the Γ point.

References

(1) Glowacki, E. D.; Voss, G.; Demirak, K.; Havlicek, M.; Sunger, N.; Okur, A. C.; Monkowius, U.; Gasiorowski, J.; Leonat, L.; Sariciftci, N. S. *Chem. Comm.* **2013**, *49*, 6063.
(2) Blanc, J.; Ross, D. L. *J. Phys. Chem.* **1968**, *72*, 2817.
(3) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, 77, 3865.
(4) Kresse, G.; Hafner, *J. Phys. Rev. B* **1993**, 47, 558.
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(6) Hafner, J.; *J. Comput. Chem.* **2008**, 29, 2044
(7) Blochl, P.E.; *Phys. Rev. B* **1994**, 50, 17953

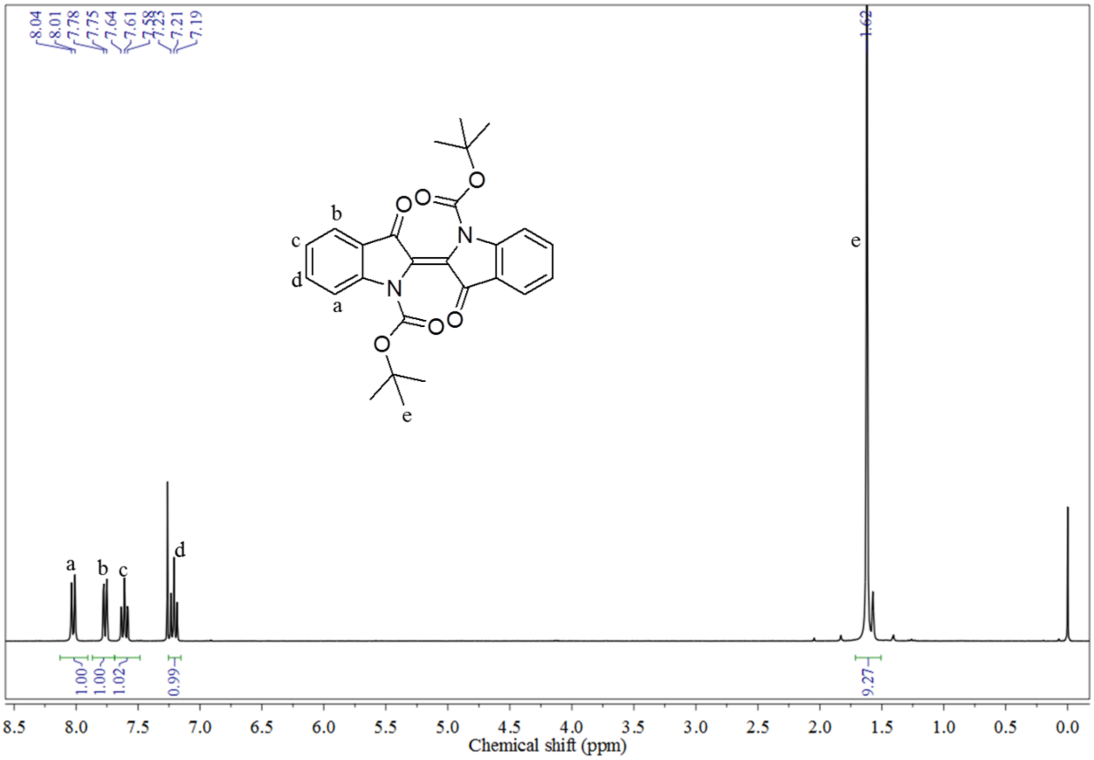

Figure S1. ^{1}H NMR (300 MHz) spectrum of Indigoid-B in $CDCl_3$.

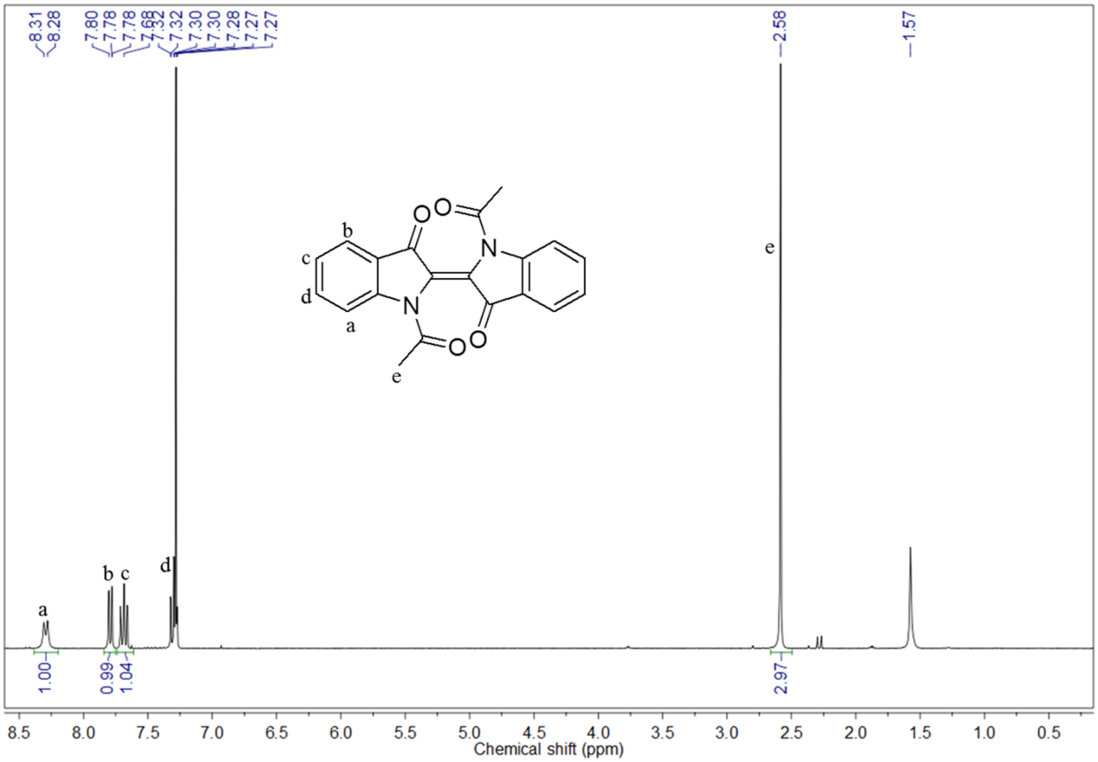

Figure S2. ^{1}H NMR(300 MHz) spectrum of Indigoid-A in $CDCl_3$.

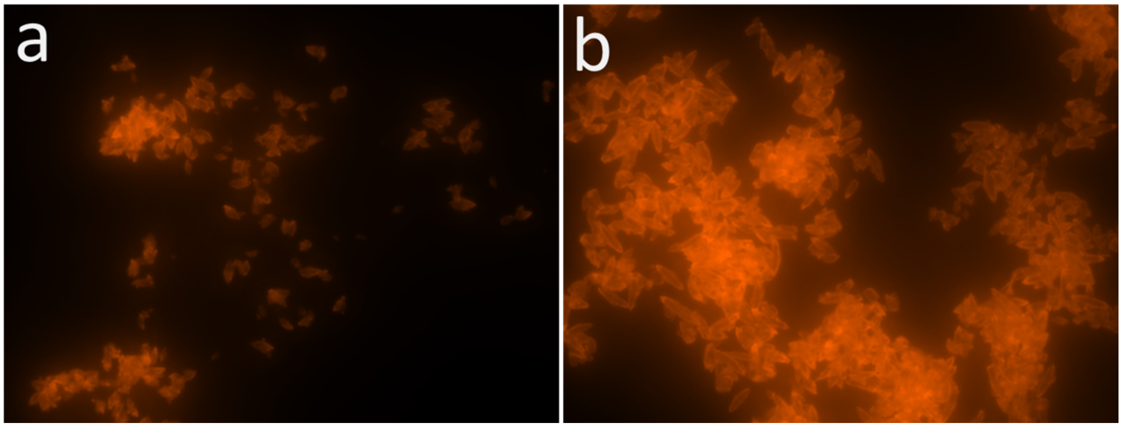

Figure S3. Fluorescence microscopic images of the octahedral microcrystals formed by Indigoid-B in THF/water mixtures. (a): f_w=80%; (b): f_w=90%. (Excitation wavelength: 488 nm)

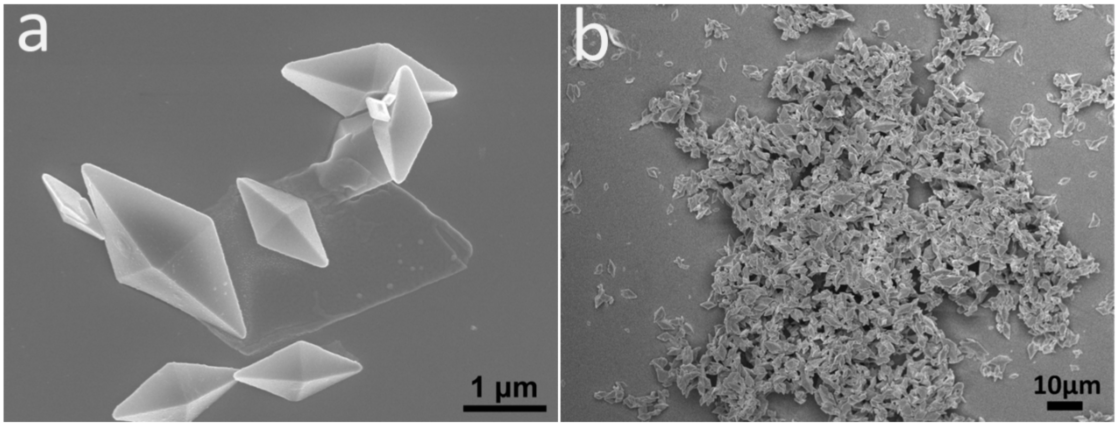

Figure S4. SEM images of the octahedral microcrystals formed by Indigoid-B in THF/water mixture (f_w=80%) with ultrasonication treatment: (a) high magnification; (b) low magnification.

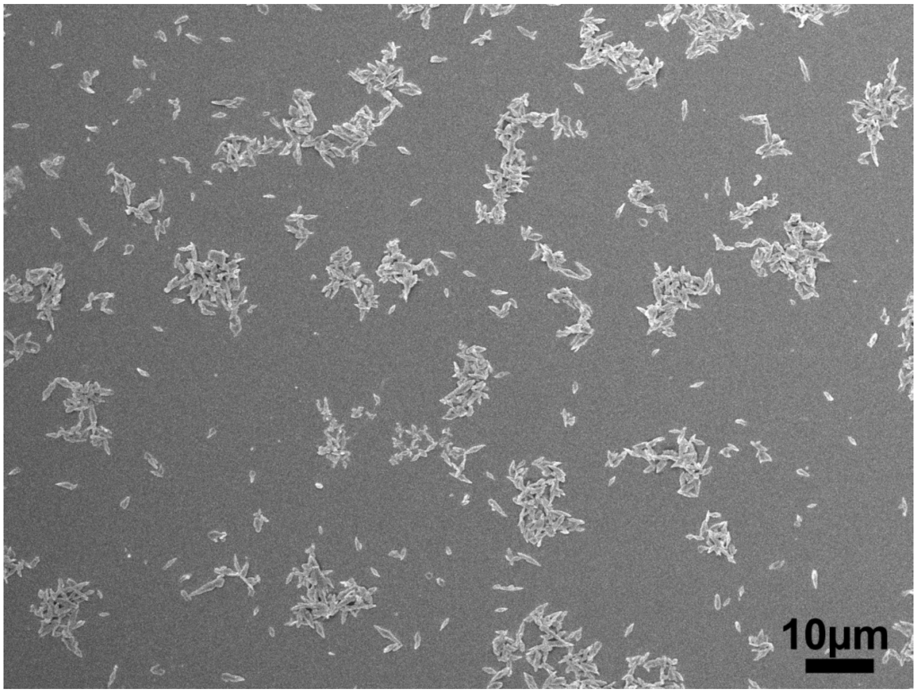

Figure S5. Low-magnification SEM image of the distorted octahedral microcrystals formed by Indigoid-B in THF/water mixture (f_w= 90%) with ultrasonication treatment.

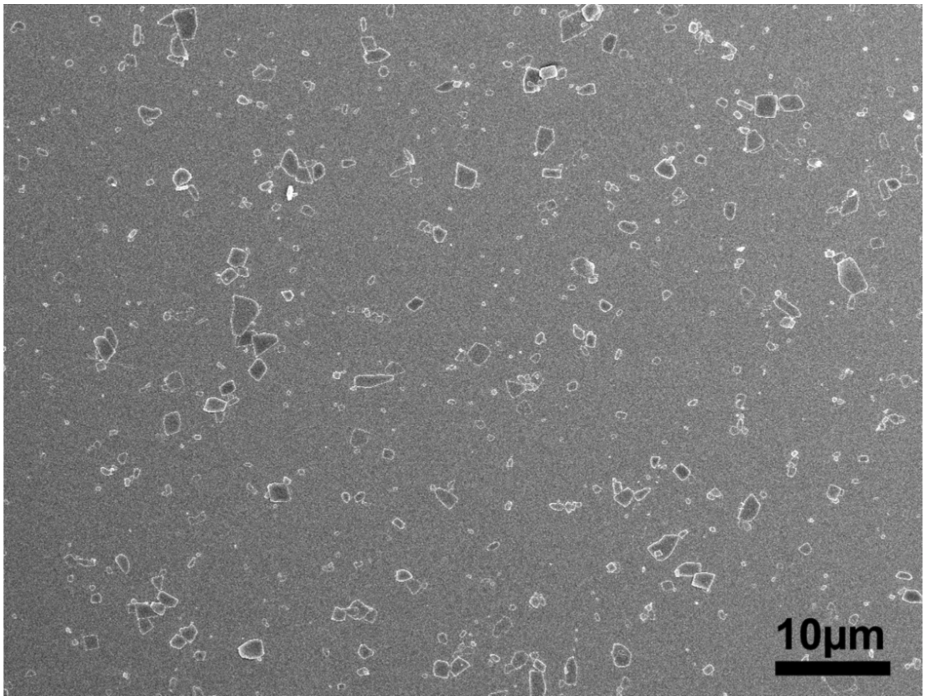

Figure S6. Low-magnification SEM image of lamellar microcrystals formed by Indigoid-B in THF/water mixture (f_w= 95%) with ultrasonication treatment.

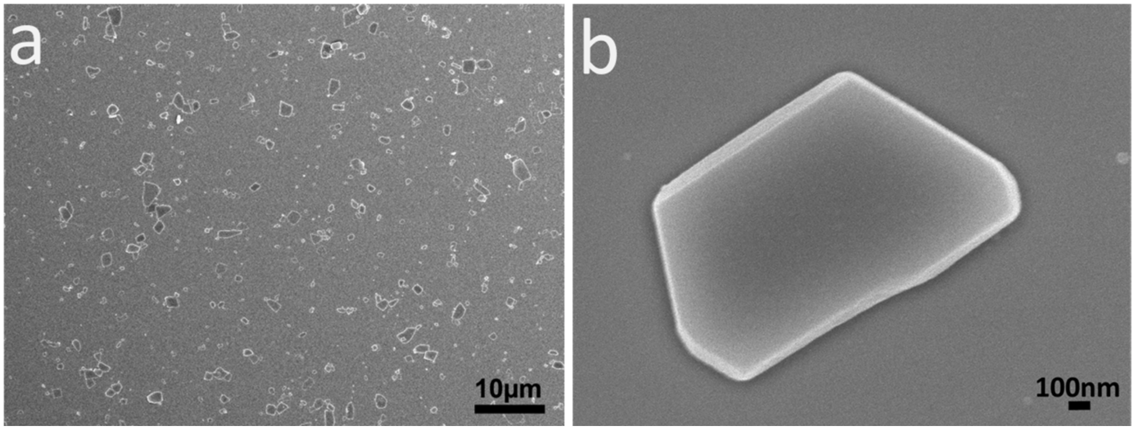

Figure S7. SEM images of the lamellar microcrystals formed by Indigoid-B in THF/water mixture (f_w= 99%) with ultrasonication treatment: (a) low magnification; (b) high magnification.

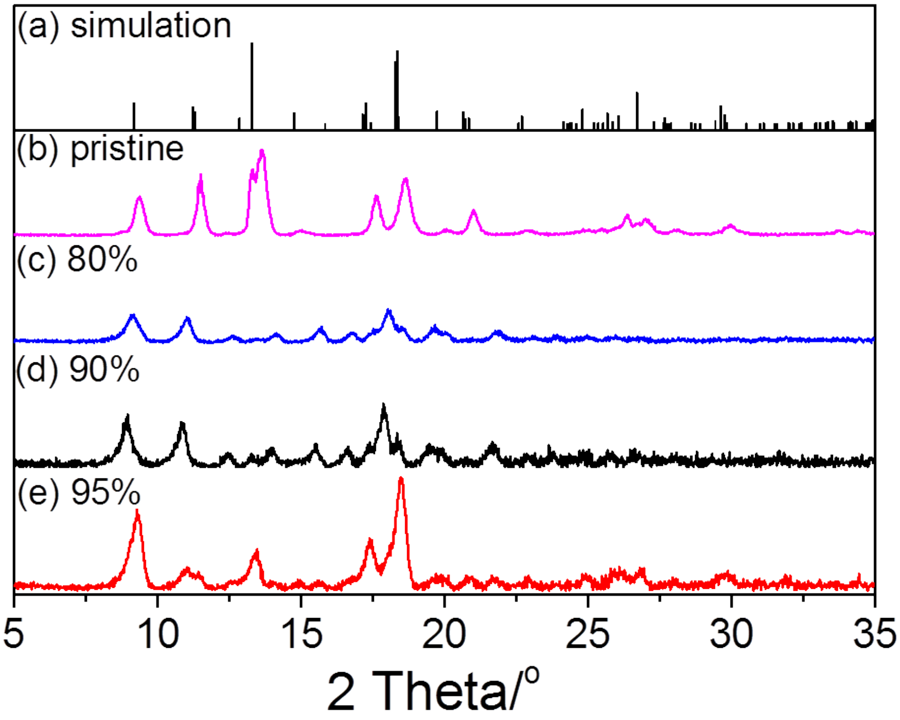

Figure S8. XRD patterns of Indigoid-B: (a) Simulated pattern of the single crystal; (b) pristine samples from recrystallization in ethyl acetate; (c-e) samples of Indigoid-B microcrystals in THF/water mixture with ultrasonication treatment: (c) f_w = 80%; (d) f_w = 90%; (e) f_w = 95%

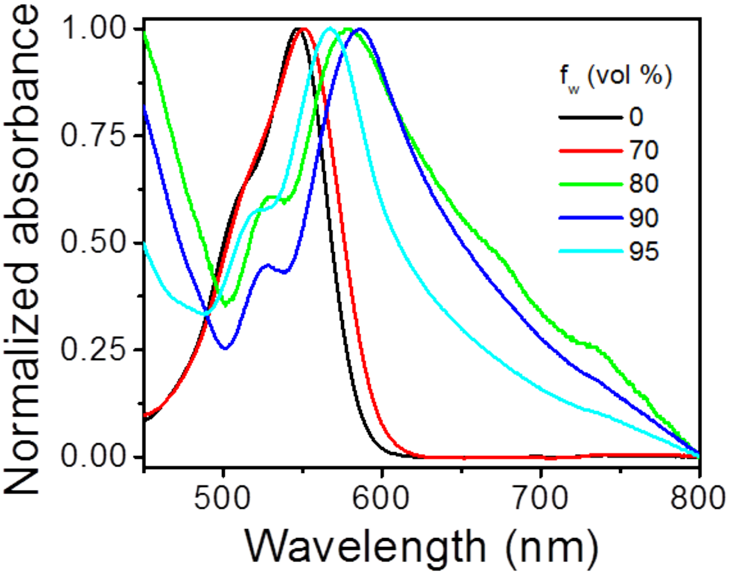

Figure S9. Normalized UV-vis absorption spectra of Indigoid-B (100 μM) in THF/water mixtures with ultrasonication treatment.

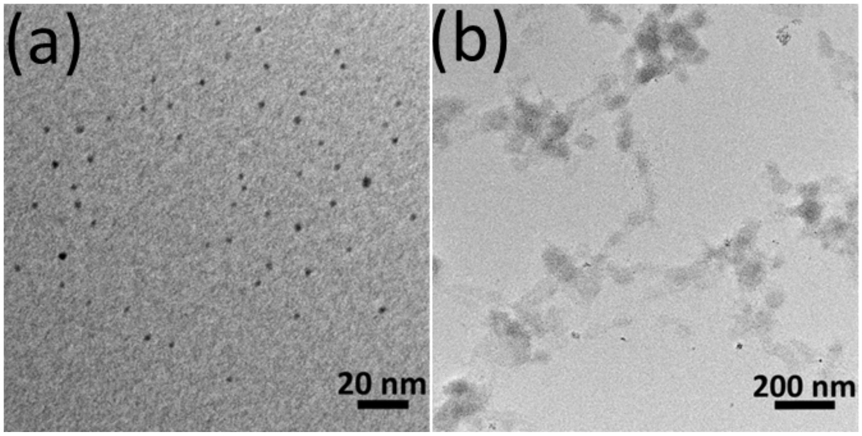

Figure S10. TEM images of Indigoid-B aggregates in THF/water mixture without ultrasonication treatment (a) $f_w = 90\%$; (b) $f_w = 95\%$.

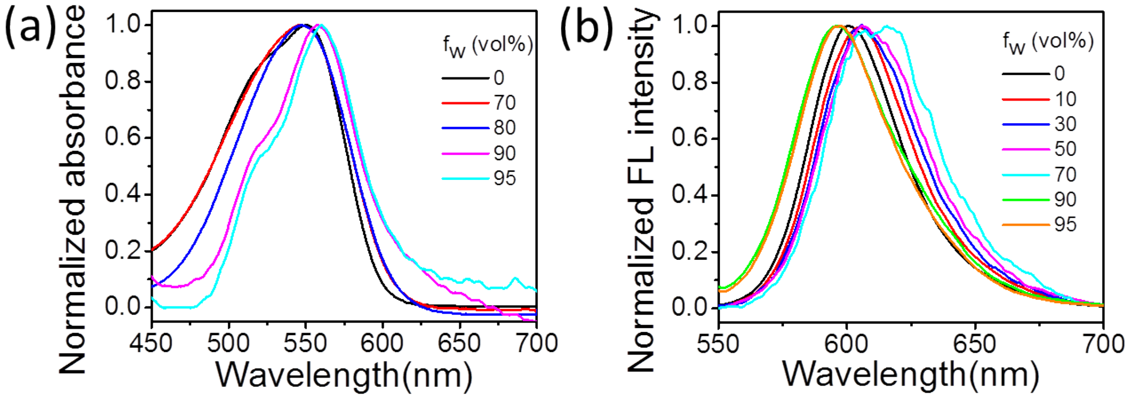

Figure S11. Normalized UV-vis absorption (a) and FL emission (b) spectra of Indigoid-A (100 μM) in THF/water mixture with ultrasonication treatment. (Excitation wavelength: 540 nm).

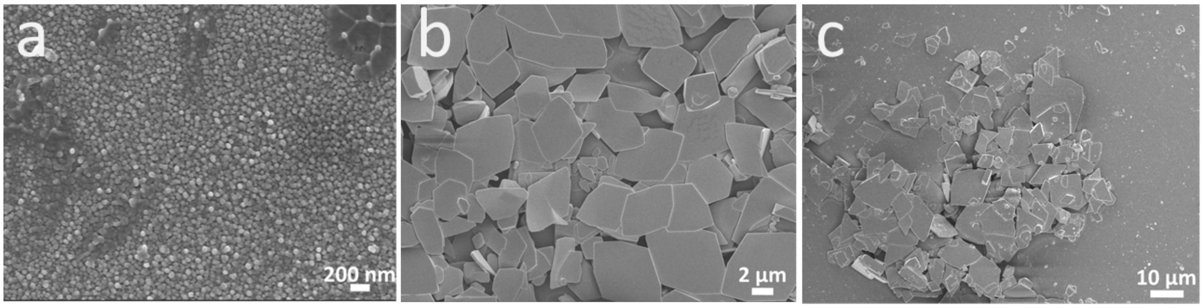

Figure S12. SEM images of Indigoid-A aggregates in THF/water mixture under ultrasonication treatment and with different water fractions: (a) 80%; (b) 90%; (c) 95%.

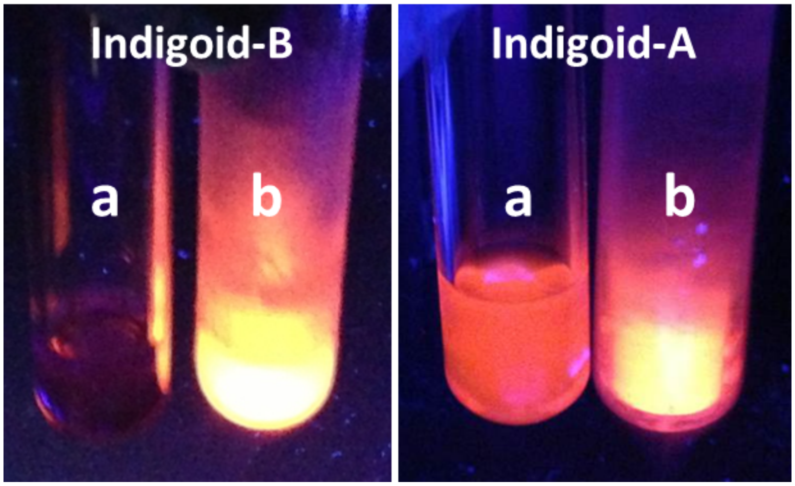

Figure S13 Digital photographs of Indigoid-B and Indigoid-A in THF solution under UV light (365 nm) irradiation at different temperatures: (a) RT; (b) -196℃ (liquid nitrogen).

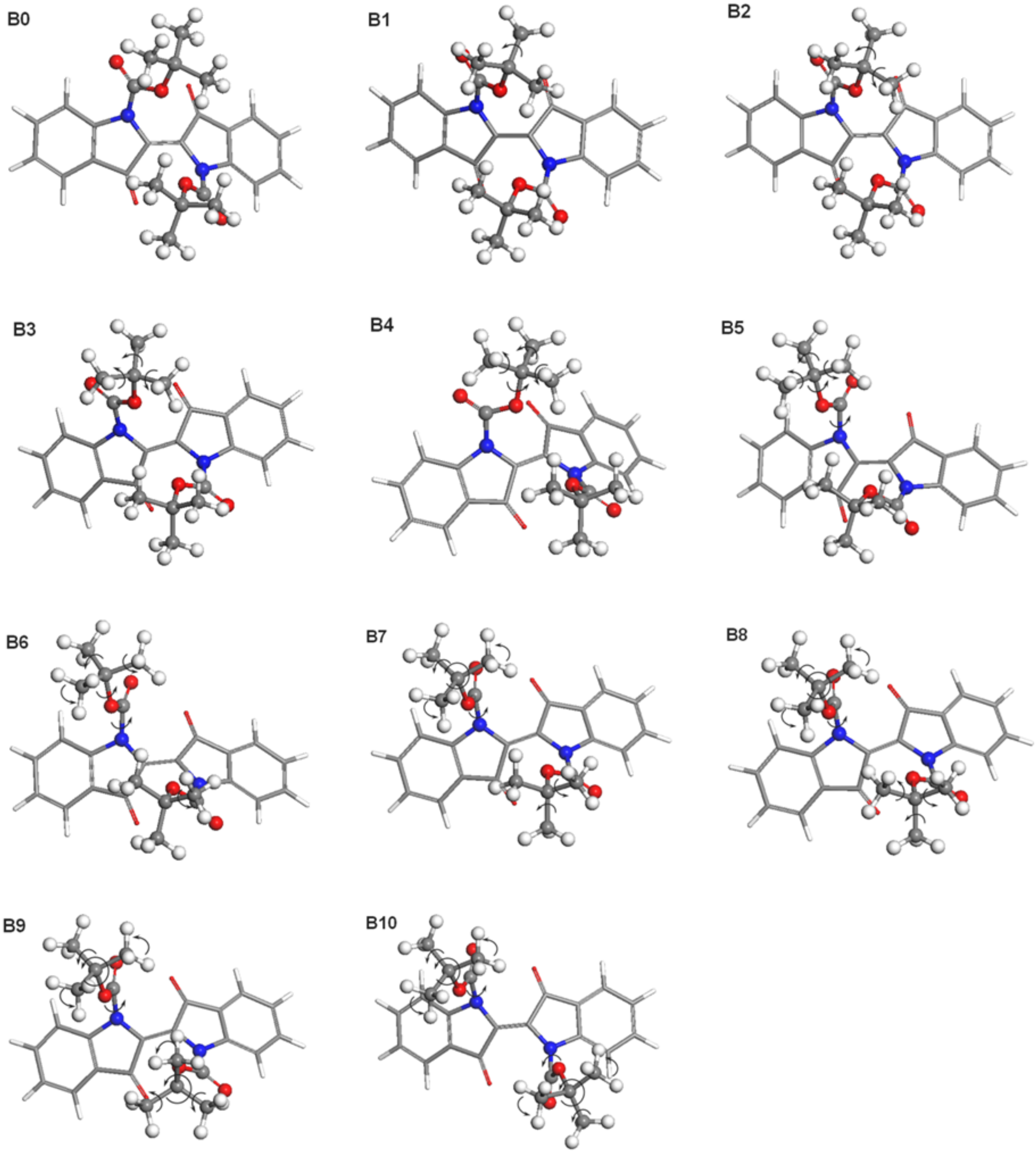

Figure S14. Different torsional configurations of Indigoid-B, as shown in Fig.4 in the paper. Inserted arrows indicate the types of torsion.

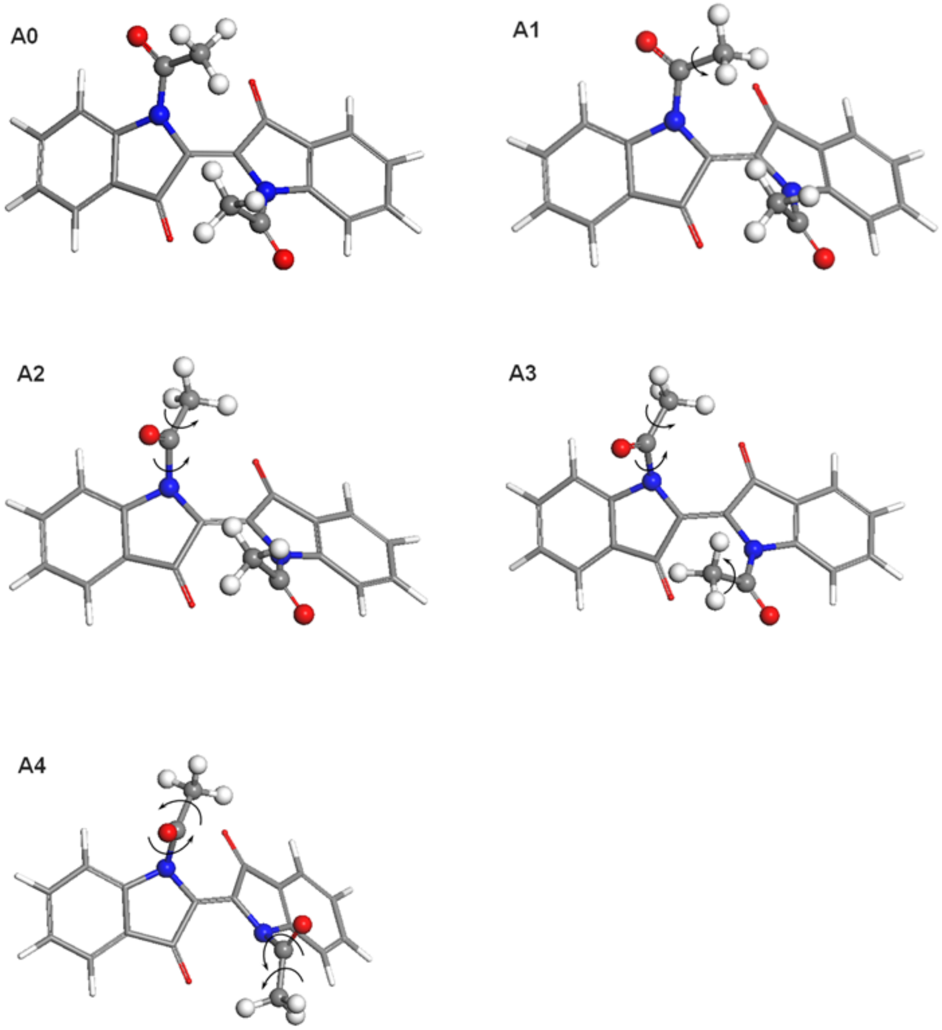

Figure S15. Different torsional configurations for Indigoid-A, as shown in Fig.4 in the paper. Inserted arrows indicate the types of torsion.

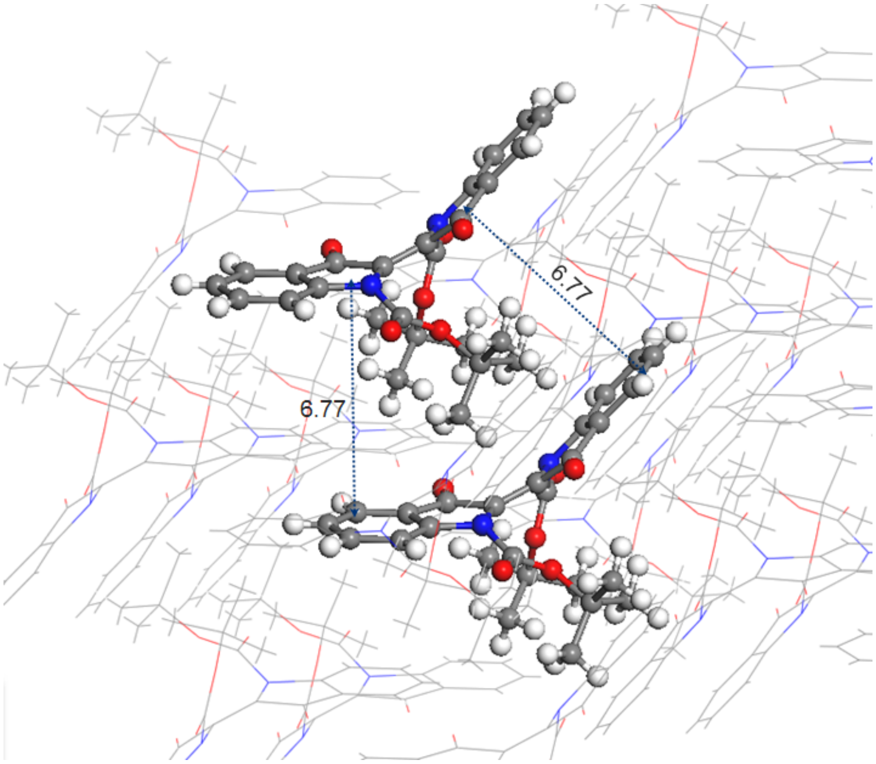

Figure S16. No π-π interaction between continuous molecules of Indigoid-B in the crystalline structure[1]. The distance between parallel π-planes is 6.77 Å.

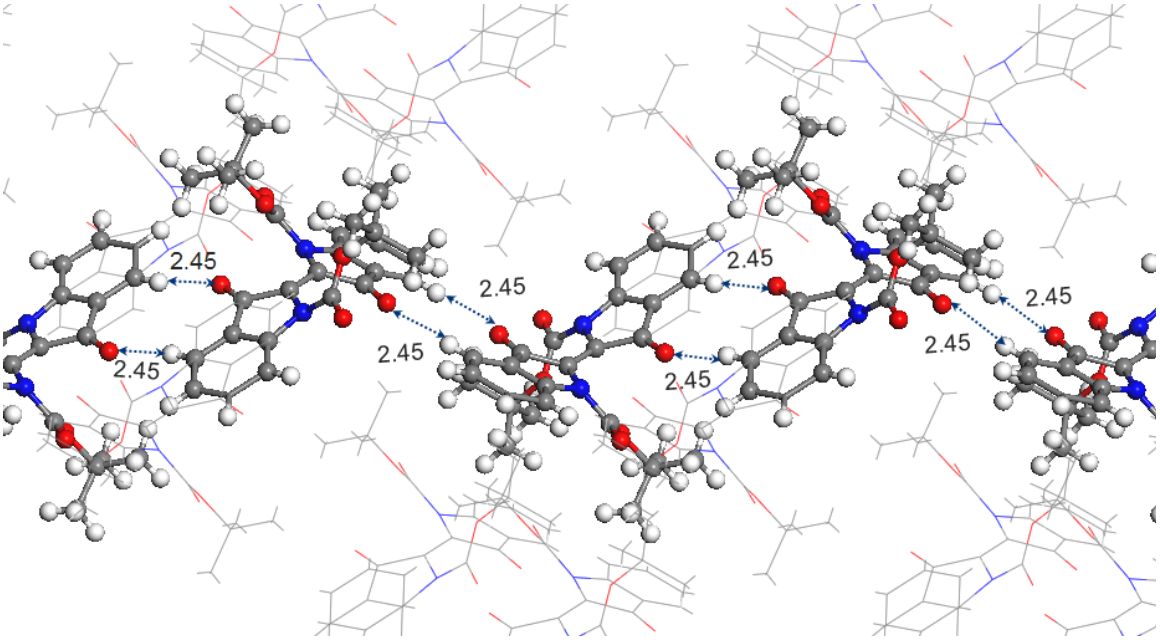

Figure S17. The zig-zag intermolecular H-bonding between adjacent molecules of Indigoid-B in the crystalline structure. Each monomer links with two adjacent molecules via 4 H-bonds, with the bond length of 2.45 Å.

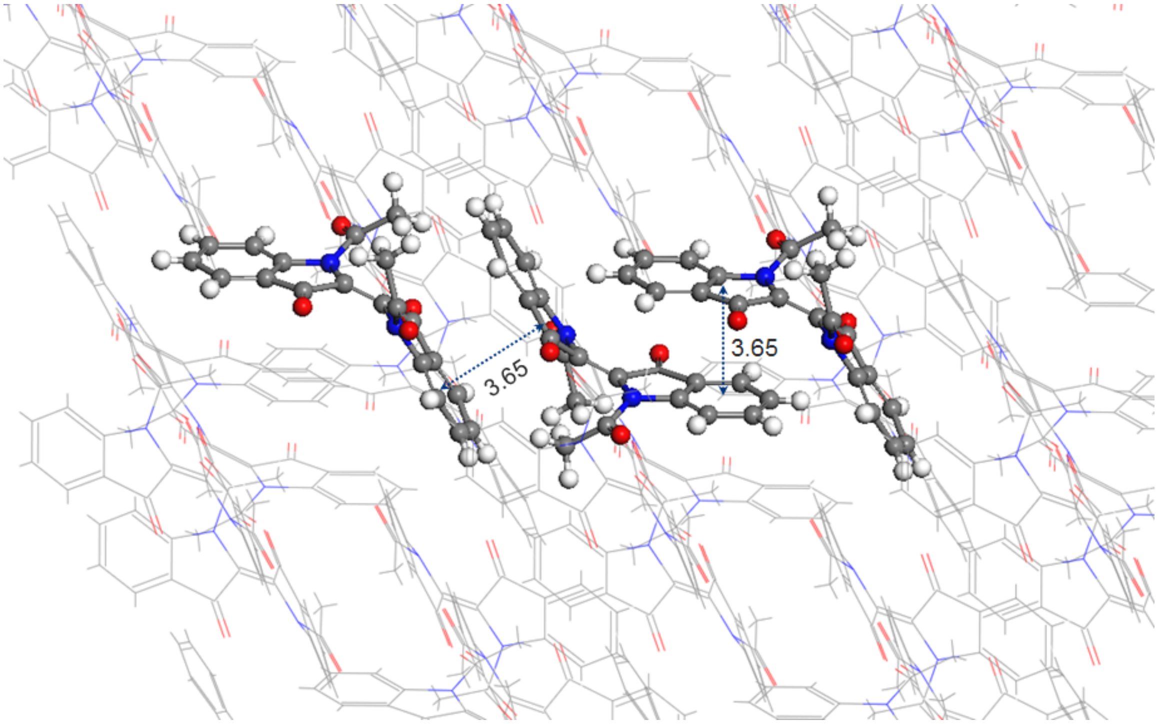

Figure S18. The "head-to-tail" π-π interaction between adjacent momoners of Indigoid-A in the crystalline state (from Cambridge Crystallographic Data Centre). The distance between parallel π-planes is 3.65 Å.

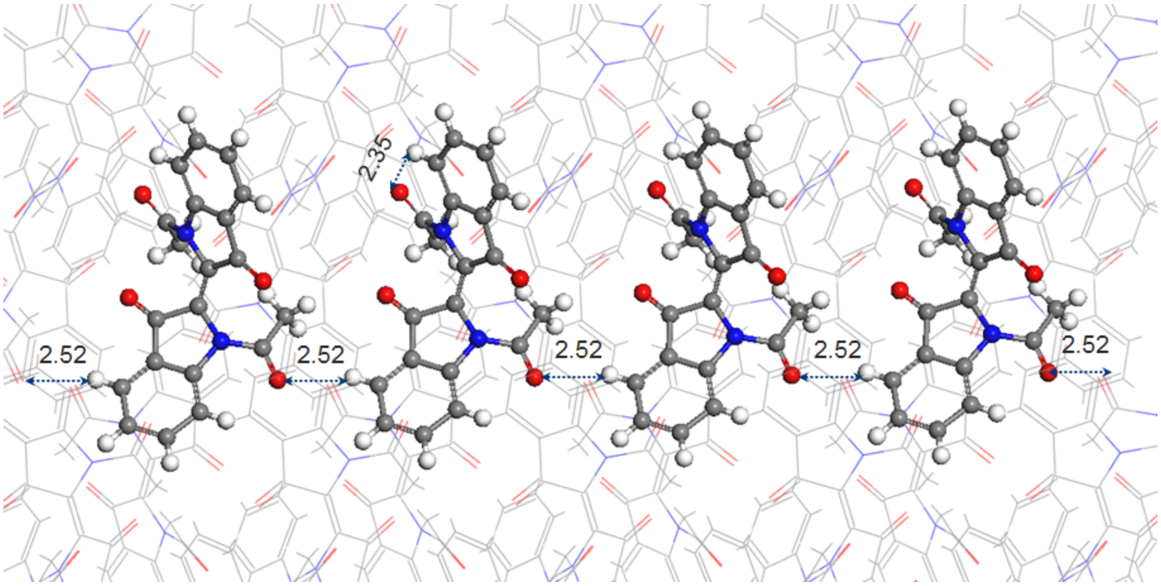

Figure S19. The intermolecular H-bonding between adjacent molecules of Indigoid-A in the crystalline structure. Each monomer links with two adjacent molecules via 2 H-bonds, with bond length of 2.52 Å.