

Supplementary data for

Photophysics of charge transfer cocrystals composed of fluorene and its heterocyclic analogues as donors and TCNQ as an acceptor

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Experimental section

Materials and general methods

Fluorene (FR), carbazole (CZ), dibenzofuran (DBF), dibenzothiophene (DBT), 7,7,8,8-tetracyanoquinodimethane (TCNQ) and solvents were purchased from commercial sources without further purification. Powder X-ray diffraction (PXRD) were carried out utilizing a Rigaku Mini Flex 600 with Cu K α radiation ($\lambda = 1.541862 \text{ \AA}$) generated at 40 kV and 150 mA. The simulated PXRD patterns were obtained from the crystallographic information file (cif) of each cocrystal by Mercury software available free of charge via the internet at <http://www.iucr.org>. Fourier transform infrared (FT-IR) spectra were collected by a Bruker VERTEX 70 spectrometer with KBr pellets. Differential scanning calorimetry (DSC) was recorded on a Netzsch DSC 200F3 instrument. Thermogravimetric analysis (TGA) was performed using a Netzsch TG 209F3 instrument. UV–vis absorption spectra were recorded on a Shimadzu UV-2600 spectrometer using an integrating sphere with BaSO₄ as white standard. Photoluminescence emissions were measured with a Hitachi FL-7000 spectrometer. Photoluminescence quantum yields (Φ_{PL}) were recorded on an Edinburgh FLS1000 instrument equipped an integrating sphere with excitation wavelength at 365 nm. Fluorescence lifetime decays were detected by a PicoQuant Microtime 200 imager with fluorescence lifetime imaging (FLIM) system equipped with a picosecond pulsed laser head by excitation source of 375 nm. Fluorescence microscopy images were taken by a Nikon DS-Ri1/ECLIPSE upright and inverted fluorescence microscope. Hirshfeld surfaces and 2D fingerprint plots of cocrystals were constructed using Crystal Explorer

17 program. The molecular orbital and energy levels of cocrystals and individual components were calculated based on crystal structures by Gaussian 09 program at the B3LYP/6-31G (d) level of theory.^{1,2}

Preparation of C1 (1:1)

Equimolar FR (16.6 mg, 0.1 mmol) and TCNQ (20.4 mg, 0.1 mmol) were added into 1 mL of acetonitrile and then suspended under room temperature for 24 h. The red powder was harvested by filtration with a yield of 73%. After about a week, rod-shaped red single crystals were obtained by evaporation of the above filtrate.

Preparation of C2 (1:1)

Equimolar CZ (16.7 mg, 0.1 mmol) and TCNQ (20.4 mg, 0.1 mmol) were added into 1 mL of acetonitrile and then suspended under room temperature for 24 h. The black powder was harvested by filtration with a yield of 91%.

Preparation of C3 (1:1)

Equimolar DBF (16.8 mg, 0.1 mmol) and TCNQ (20.4 mg, 0.1 mmol) were added into 1 mL of acetonitrile and then suspended under room temperature for 24 h. The red powder was harvested by filtration with a yield of 82%. After about a week, rod-shaped red single crystals were obtained by evaporation of the above filtrate.

Preparation of C4 (1:1)

Equimolar DBT (18.4 mg, 0.1 mmol) and TCNQ (20.4 mg, 0.1 mmol) were added into 1 mL of acetonitrile and then suspended under room temperature for 24 h. The red powder was harvested by filtration with a yield of 76%. After about a week, rod-shaped red single crystals were obtained by evaporation of the above filtrate.

Single crystal X-ray diffraction

Single X-ray diffraction data were recorded on an Agilent Technologies Gemini A Ultra system with graphite monochromated Cu K α radiation ($\lambda = 1.54178 \text{ \AA}$). Cell refinement and data reduction were applied using the program CrysAlis^{PRO}. Single X-ray diffraction data were analyzed by direct methods using Olex2 program and refined by the full-matrix least-squares method on F^2 .³ Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions with fixed isotropic thermal parameters and included in the structure factor calculations in the final stage of full-matrix least-squares refinement.

References

- 1 M. Frisch, G. Trucks and H. J. I. Schlegel, Wallingford CT. G09: Rev C. 01, Gaussian, 2013.
- 2 T. J. Penfold and G. A Worth, *Chem. Phys.*, 2010, **375**, 58–66.
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Table S1 Molecular geometry of the TCNQ molecule in cocrystals and estimate of the degree of charge transfer

	a (Å)	b (Å)	c (Å)	d (Å)	α^a	ρ^b
TCNQ	1.346	1.445	1.374	1.441	0.476	
C1	1.337	1.444	1.369	1.432	0.476	0.03
C2	1.390	1.389	1.419	1.405	0.508	0.25
C3	1.342	1.443	1.372	1.433	0.477	0.07
C4	1.346	1.441	1.375	1.431	0.479	0.13
TCNQ ⁻	1.375	1.481	1.430	1.461	0.486	

^a $\alpha = c/(b+d)$

$${}^b \rho = \frac{\alpha_{CT} - \alpha_0}{\alpha_{-1} - \alpha_0}$$

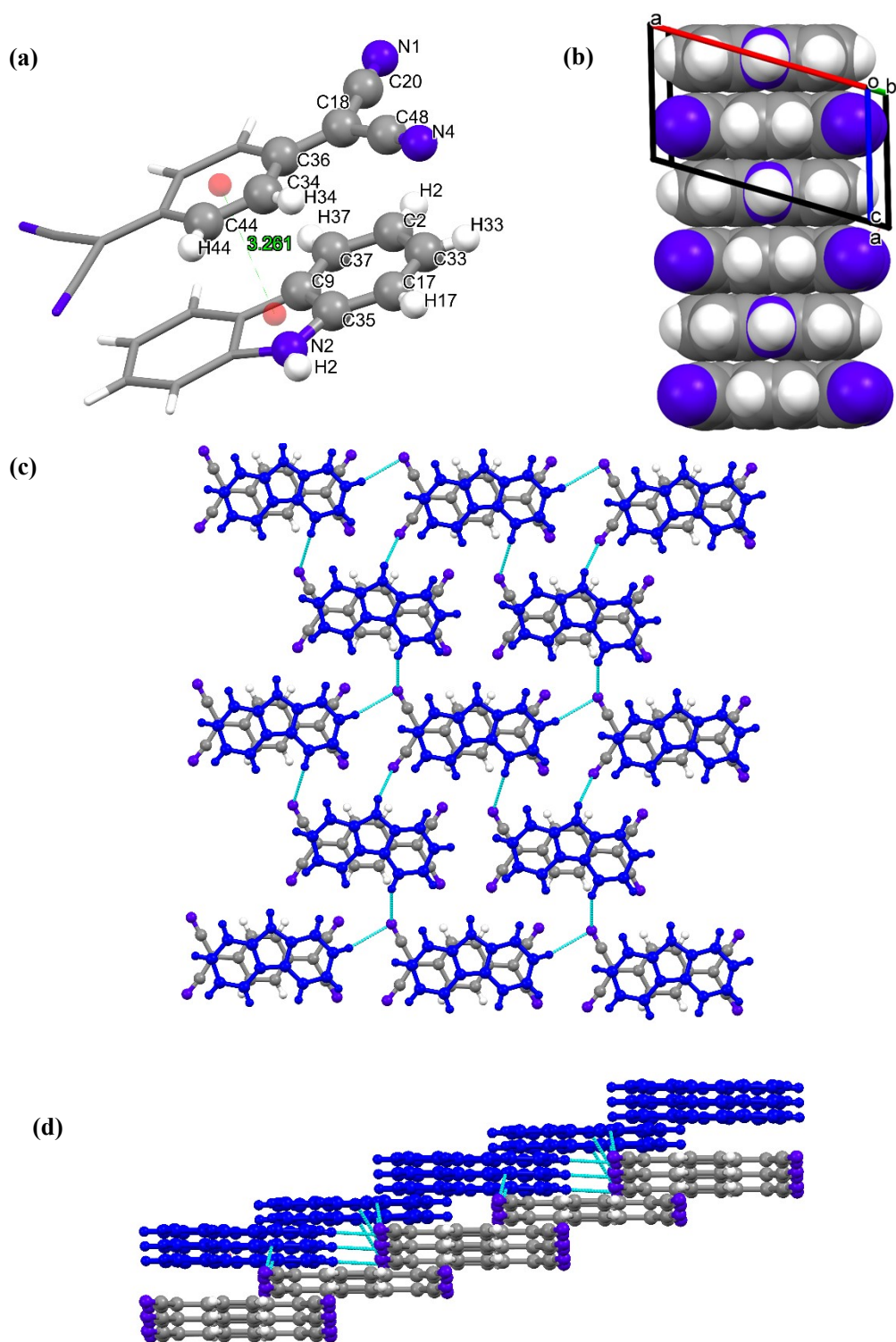


Fig. S1 (a) Asymmetric unit, (b) \cdots DADADA \cdots column-like charge transfer structure, and (c) top view and (d) side view of 3D structure of cocystal C2.

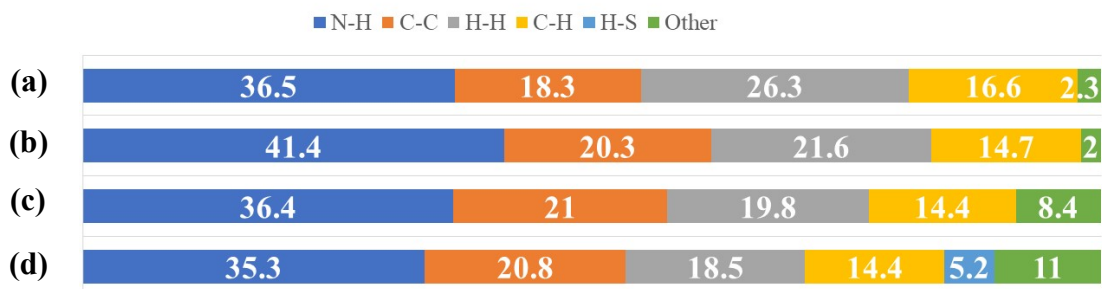


Fig. S2 Relative contributions of various intermolecular contacts to the Hirshfeld surface area for (a) C1, (b) C2, (c) C3 and (d) C4.

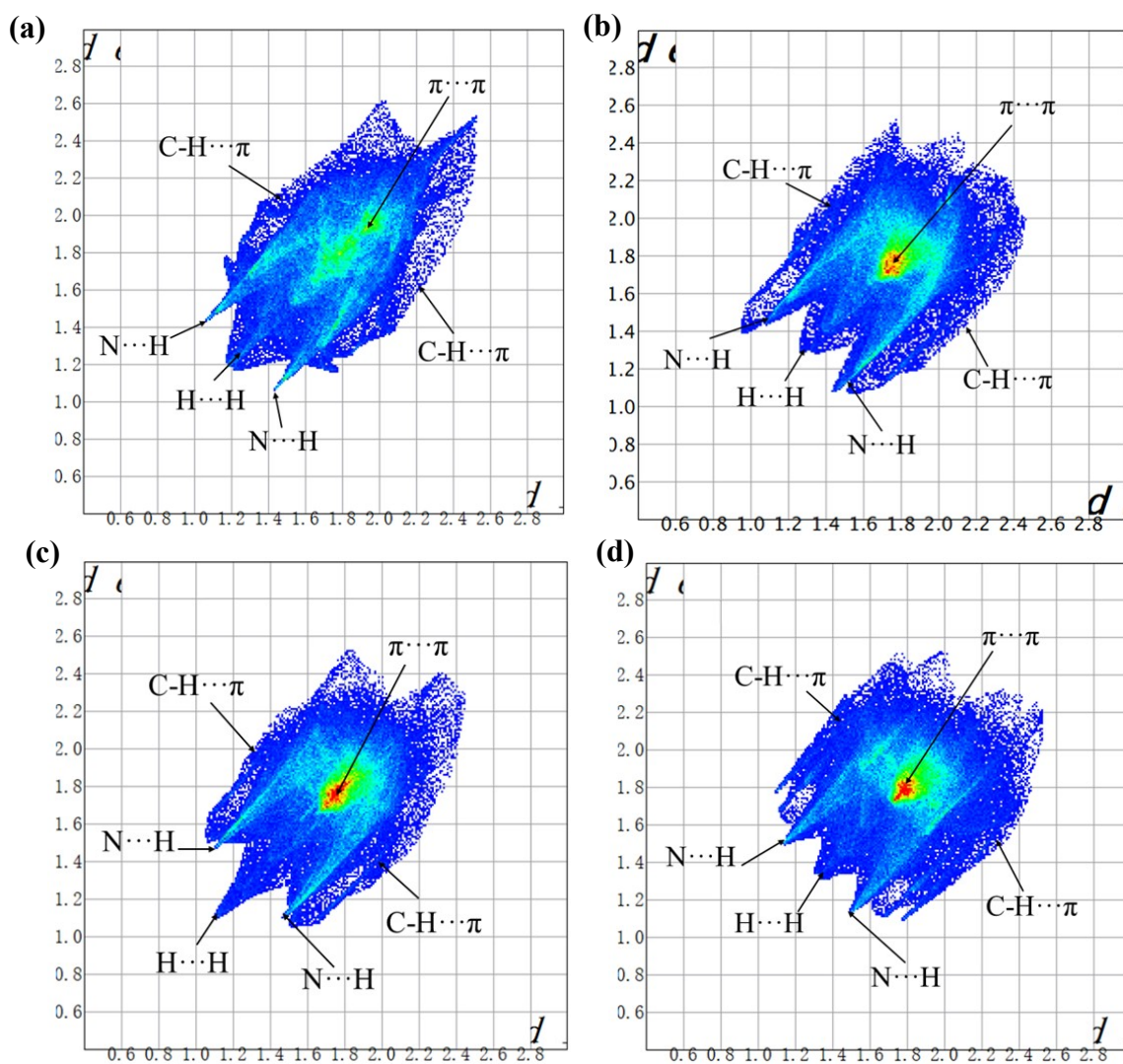


Fig. S3 Hirshfeld surface mapped with d_{norm} and 2D fingerprint plots for (a) C1, (b) C2, (c) C3 and (d) C4.

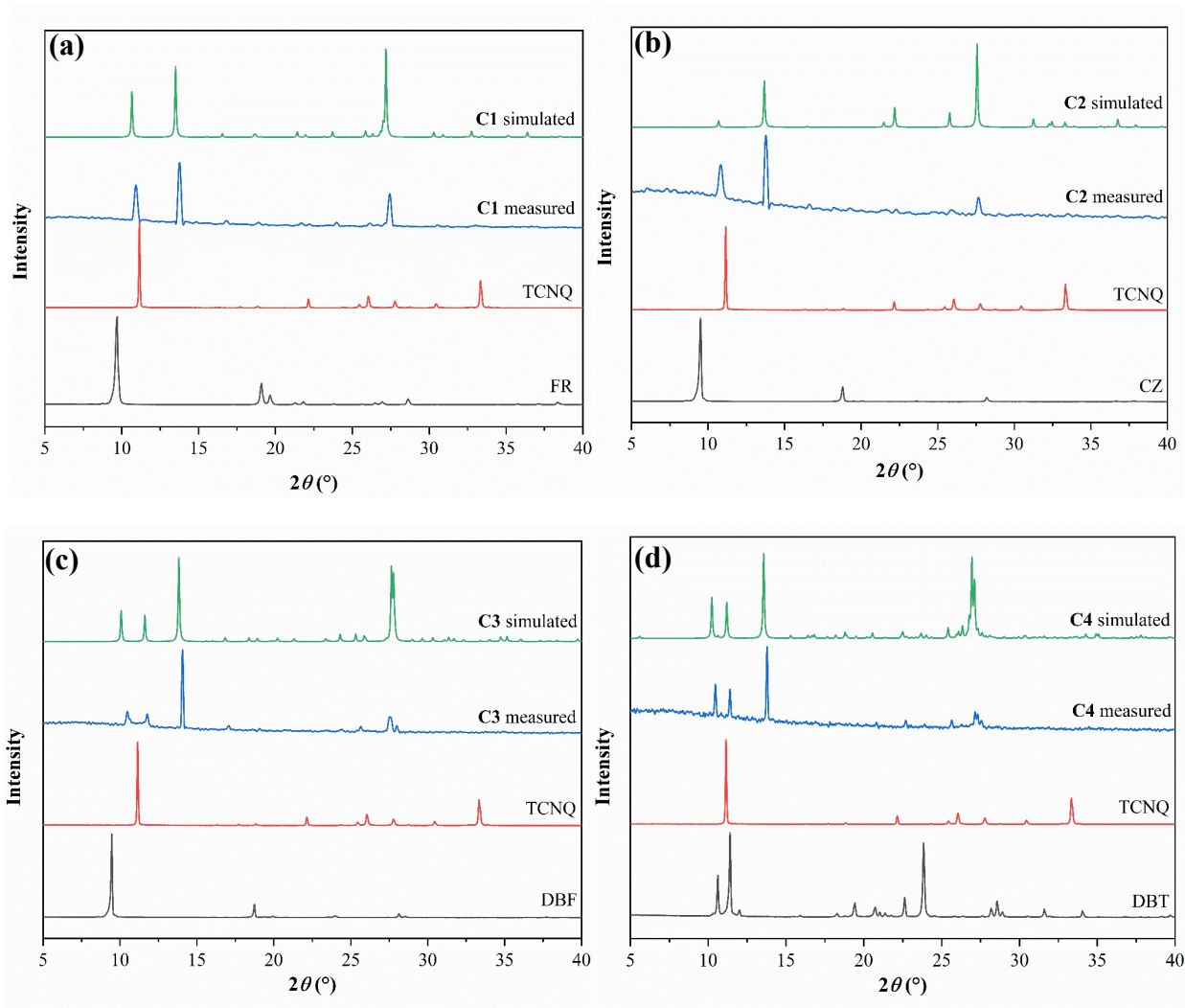


Fig. S4 Comparison of experimental and simulated PXRD patterns of the cocrystals and the corresponding single components for (a) C1, (b) C2, (c) C3 and (d) C4.

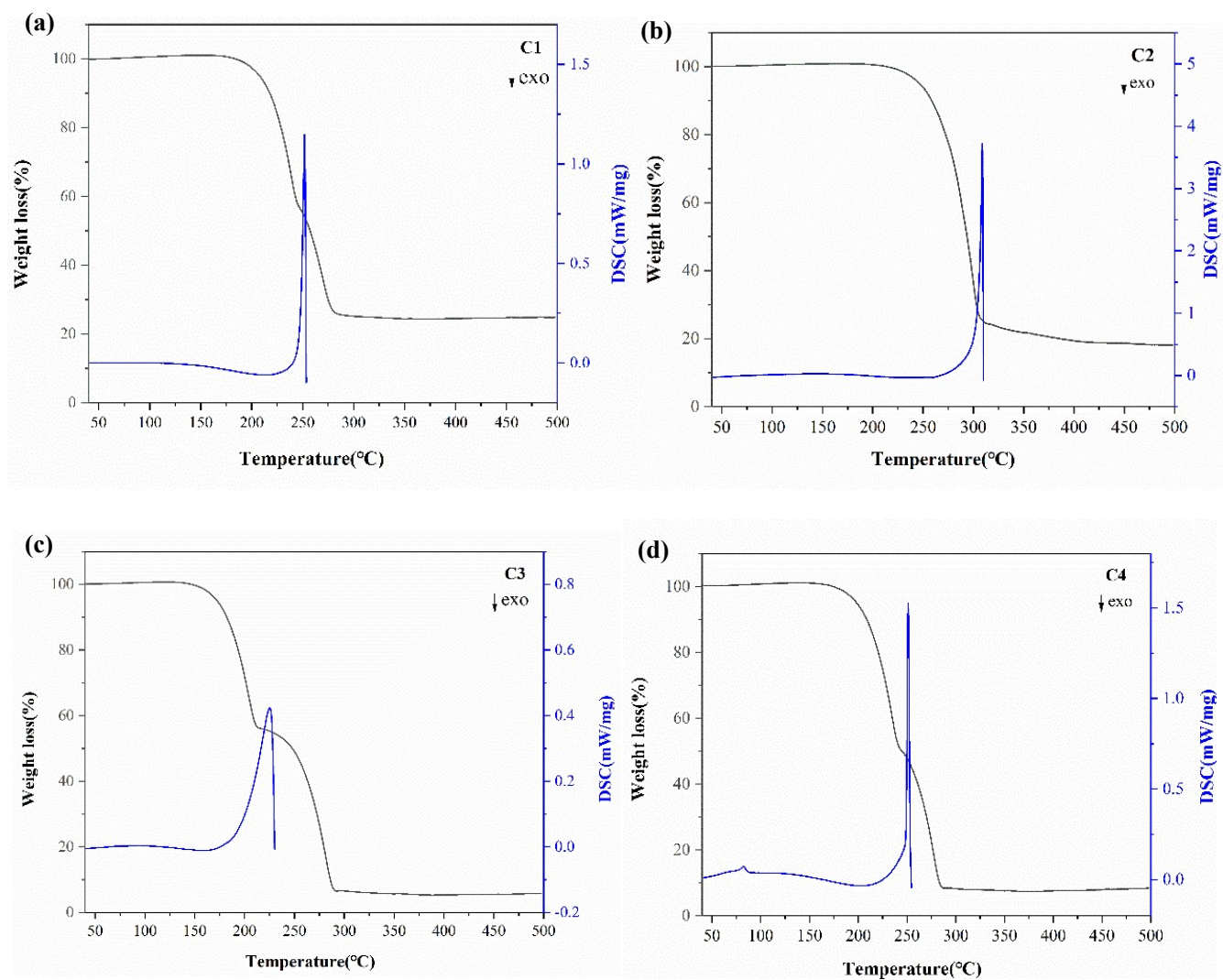


Fig. S5 TG-DSC curves of (a) C1, (b) C2, (c) C3 and (d) C4.

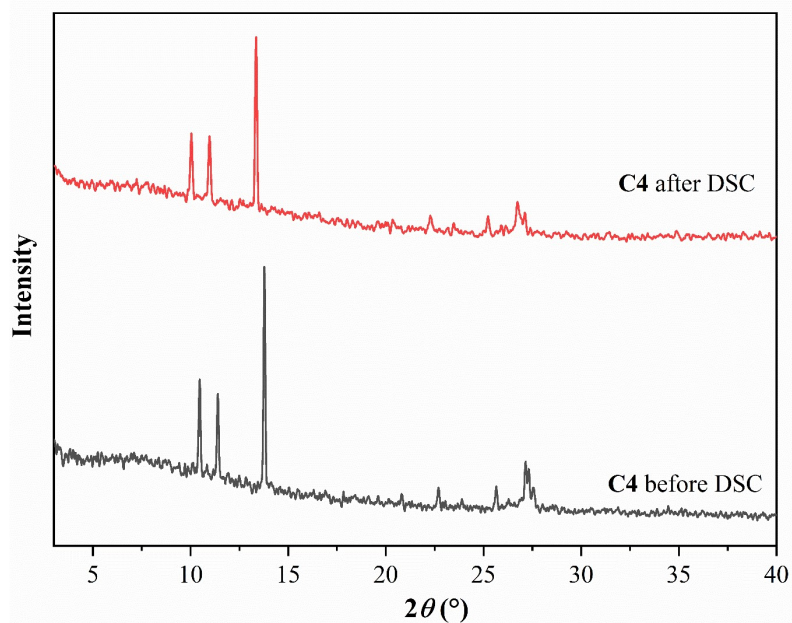


Fig. S6 PXRD patterns of C4 before and after heating to 185 °C by DSC. It demonstrates a reverse phase change process.

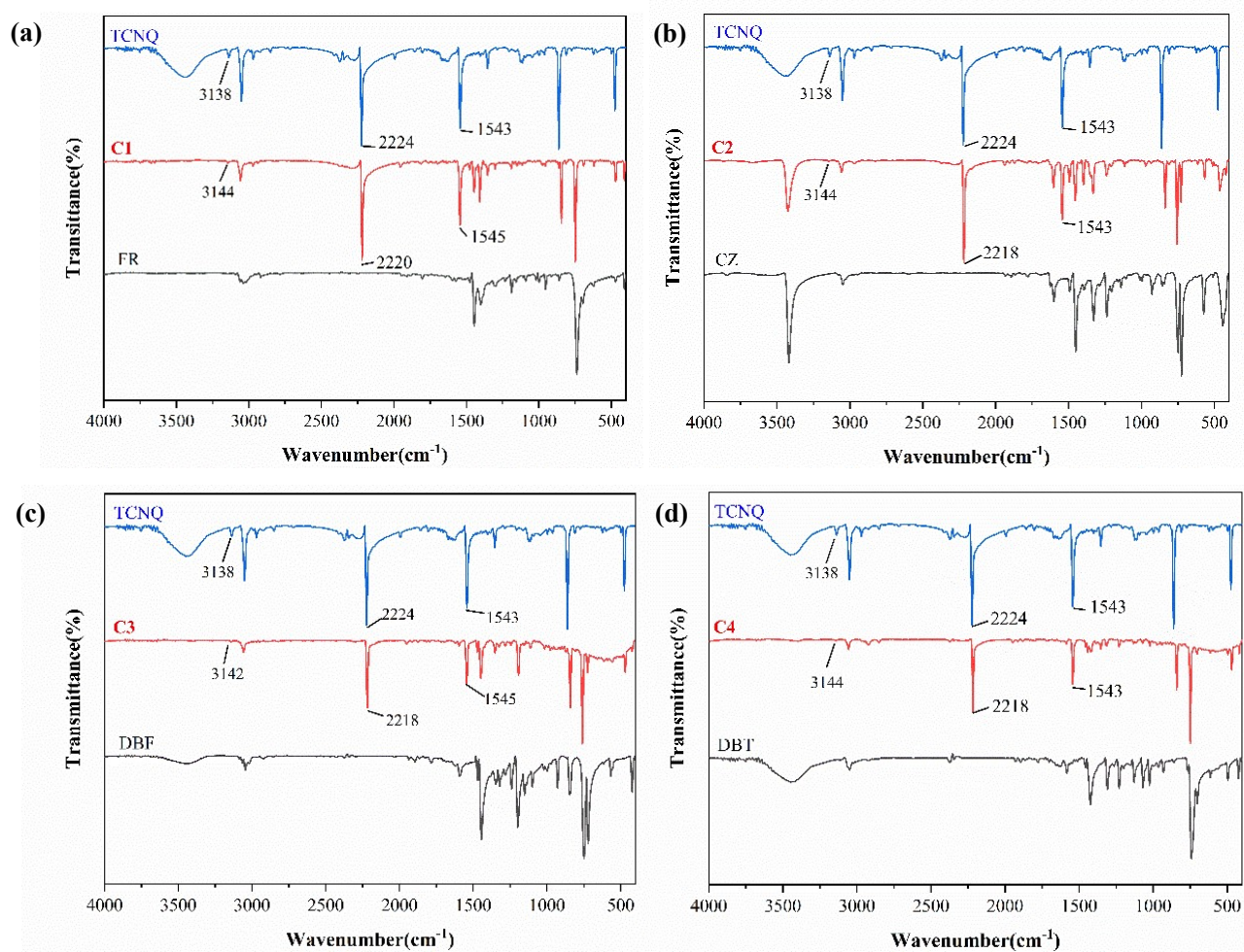


Fig. S7 FT-IR spectra of cocrystals and single components for (a) C1, (b) C2, (c) C3 and (d) C4.