Electronic Supplementary Material (ESI) for ChemComm.

Construction of a Solid-State Supramolecular Polymer Based on Host–Guest Recognition Motif between Perethylated Pillar[5]arene and Tetrathiafulvalene

Xueru Zhao,[a,b] Bin Hua,[b,c] and Li Shao*[a,b]

[a] *Department of Materials Science and Engineering Zhejiang Sci-Tech University, Hangzhou, 310018, P. R. China*

[b] *Zhejiang Provincial Innovation Center of Advanced Textile Technology, Shaoxing, 312000 P. R. China*

[c] *Stoddart Institute of Molecular Science, Department of Chemistry Zhejiang University, Hangzhou, 310058, P. R. China*

[d] *Zhejiang-Israel Joint Laboratory of Self-Assembling Functional Materials, ZJU-Hangzhou Global Scientific and Technological Innovation Center, Zhejiang University, Hangzhou, 311215, P. R. China*

Email: lishao@zstu.edu.cn

Electronic Supplementary Information (10 pages)

1. Materials and methods

All reagents were commercially available and used as supplied without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature. Compounds **EtP5**[S1] was synthesized according to previous literature. NMR spectra were recorded with a Bruker Avance DMX 600 spectrophotometer or a Bruker Avance DMX 500 spectrophotometer with the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. The fluorescence experiments were conducted on an RF-5301 spectrofluorophotometer (Shimadzu Corporation, Japan). Quantum yield measurements were performed using the absolute method on a FLS920 from Edinburgh Instruments equipped with a $BaSO_4$-coated integrating sphere, a 450W Xe900 Xenon lamp and a R928P PMT detector.

*2. ^{1}H NMR spectra of solutions of **TTF** with **EtP5***

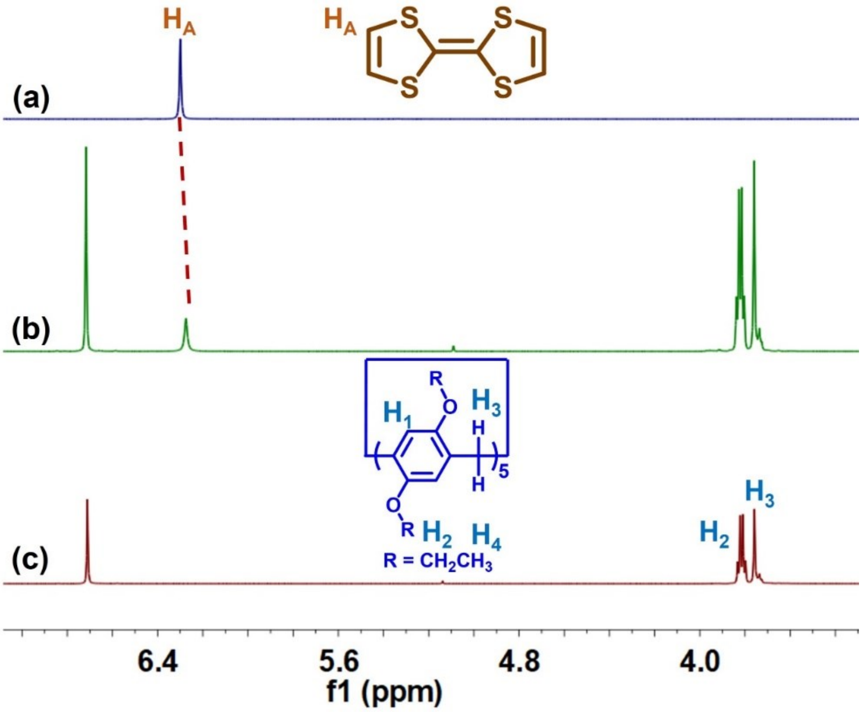

Figure S1. Partial ^{1}H NMR spectra (500 MHz, $CDCl_3$, 293 K): (a) **TTF**; (b) an equimolar (10.0 mM) solution of **TTF** and **EtP5**; (c) **EtP5**.

*3. ^{1}H NMR titration experiments for the host−guest complexation of **TTF** and with **EtP5***

To determine the stoichiometry and association constant between **EtP5** and guests **G** (**TTF**), ^{1}H NMR titration was done with solutions which had a constant concentration of **G** (1.00 mM) and varying concentrations of **EtP5**. By a non-linear curve-fitting method, the association constant between guest **G** and host **EtP5** was calculated. The non-linear curve-fitting was based on the equation:[S2]

$$\Delta\delta = (\Delta\delta_\infty/[\mathbf{G}]_0)\,(0.5[\mathbf{EtP5}]_0 + 0.5([\mathbf{G}]_0+1/K_a)-(0.5([\mathbf{EtP5}]_0^{\,2}+(2[\mathbf{EtP5}]_0(1/K_a - [\mathbf{G}]_0)) + (1/K_a + [\mathbf{G}]_0)^2)^{\,0.5})) \qquad \text{(S1)}$$

Where $\Delta\delta$ is the chemical shift change of a proton on **G** at $[\mathbf{EtP5}]_0$, $\Delta\delta_\infty$ is the chemical shift change of the proton when the guest is completely complexed, $[\mathbf{G}]_0$ is the fixed initial concentration of the guest, and $[\mathbf{EtP5}]_0$ is the varying concentrations of **EtP5**.

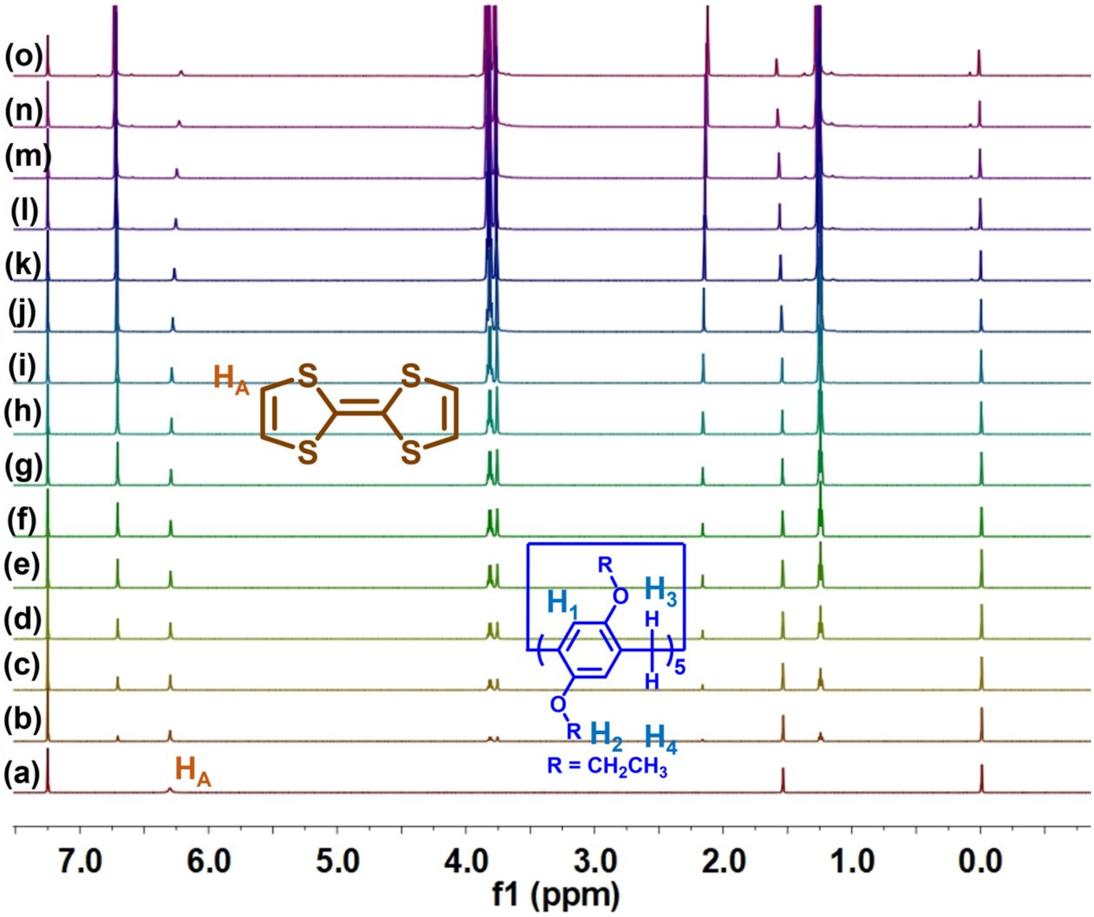

Figure S2. ^{1}H NMR spectra (600 MHz, $CDCl_3$, 293 K) of **TTF** at a concentration of 10.0 mM with different concentrations of **EtP5**: (a) 0 mM, (b) 0.96 mM, (c) 2.37 mM,

(d) 3.47 mM, (e) 4.67 mM, (f) 6.01 mM, (g) 7.51 mM, (h) 9.89 mM, (i) 12.4 mM, (j) 18.1 mM, (k) 30.7 mM, (l) 44.1 mM, (m) 49.8 mM, (n) 71.9 mM and (o) 98.2 mM.

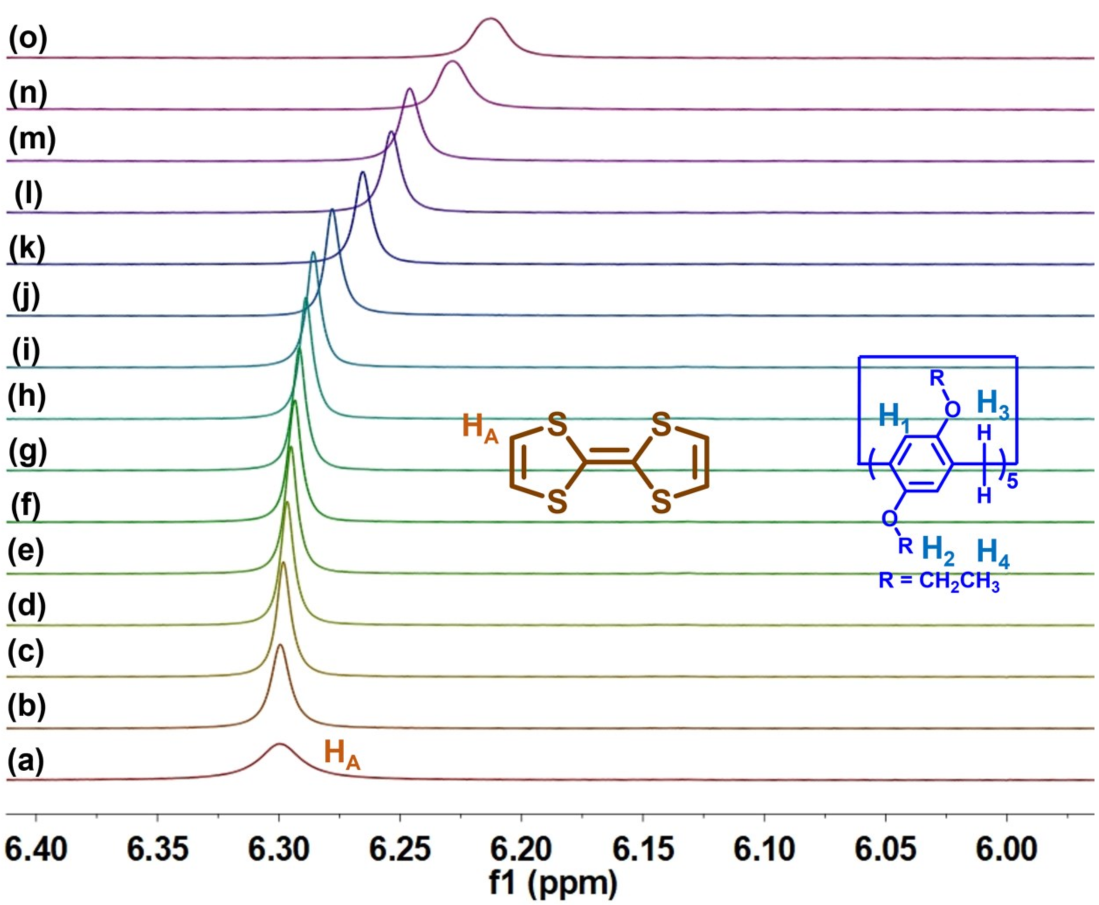

Figure S3. Partial ^{1}H NMR spectra (600 MHz, CDCl$_3$, 293 K) of **TTF** at a concentration of 10.0 mM with different concentrations of **EtP5**: (a) 0 mM, (b) 0.96 mM, (c) 2.37 mM, (d) 3.47 mM, (e) 4.67 mM, (f) 6.01 mM, (g) 7.51 mM, (h) 9.89 mM, (i) 12.4 mM, (j) 18.1 mM, (k) 30.7 mM, (l) 44.1 mM, (m) 49.8 mM, (n) 71.9 mM and (o) 98.2 mM.

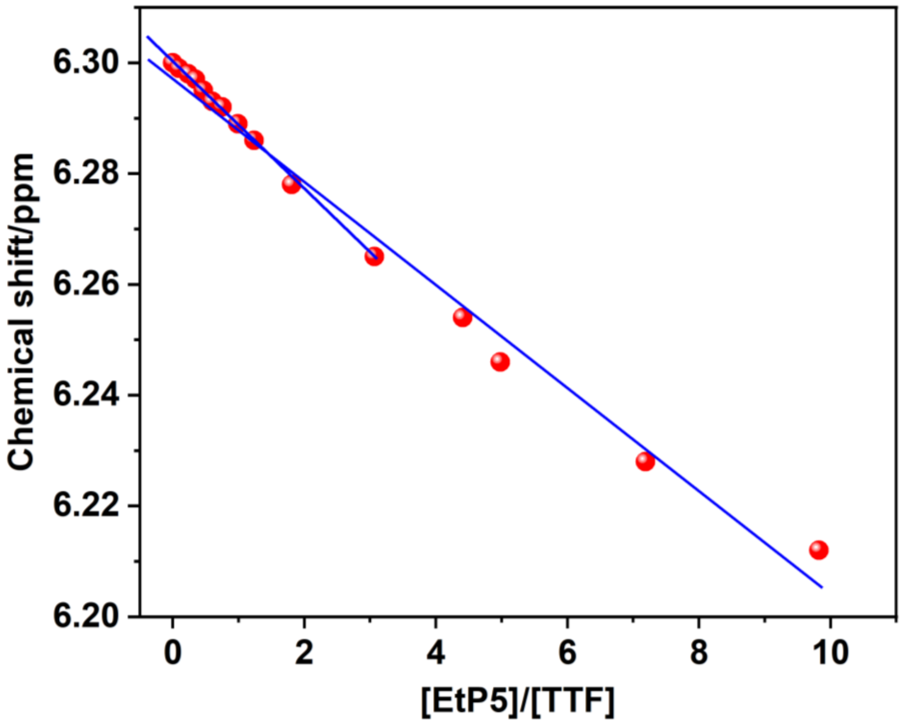

Figure S4. Molar ratio plot for the complexation between **EtP5** and **TTF** in $CDCl_3$, indicating an approximate 1:1 binding stoichiometry.

The line was fitted by equation y = a + b*x, the first line was fitted with x range from 0 to 0.5, where a = 6.300 ± 0.0002 , b = –0.011 ± 0.0004, R^2 = 0.99; the second line was fitted with x range from 0.5 to 11, where a = 6.297 ± 0.0013, b = –0.009 ± 0.0003, R^2 = 0.987. The crosspoint is x = 1.3, y = 6.3, indicating that the molar ratio of [**EtP5**]/[**TTF**] = 1.3 is the binding stoichiometry.

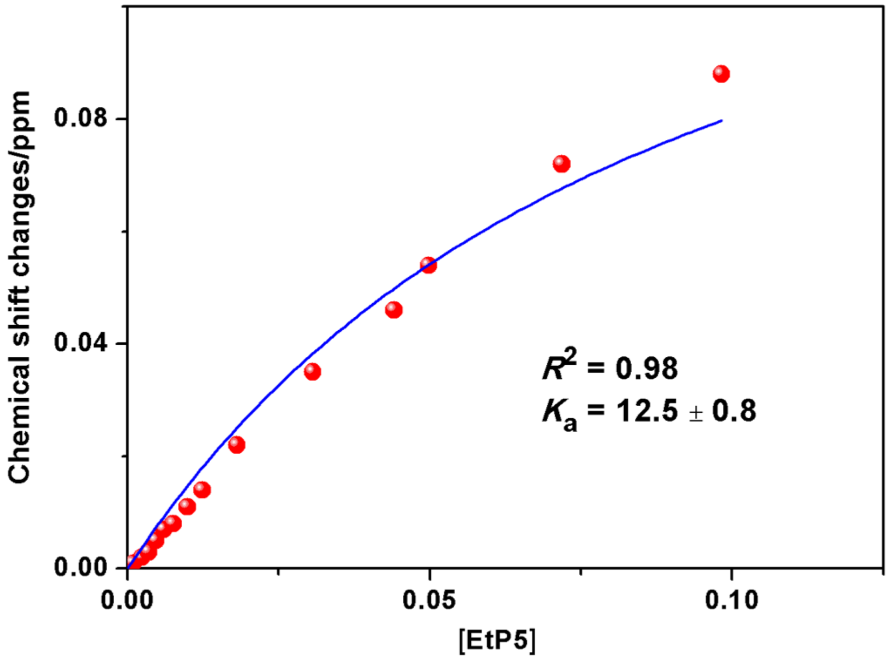

Figure S5. The chemical shift changes of H_A on **TTF** upon addition of **EtP5** in $CDCl_3$. The blue solid line was obtained from the non-linear curve-fitting using Eq. S1.

*4. X-ray crystal data of **EtP5⊃TTF***

Formula	**EtP5⊃TTF**
Collection Temperature	193 K
Sum Formula	$C_{61}H_{74}O_{10}S_4$
Mr	1095.44
Crystal System	Monoclinic
Space Group	C2/c
a [Å]	21.590 (4)
b [Å]	20.575 (3)
c [Å]	13.578 (2)
α [°]	90
β [°]	97.516(5)
γ [°]	90
V [Å3]	5979.9 (17)
Z	4
D*calcd* [g cm-3]	1.217
μ[mm-1]	0.214

F(000)	2336.0
2θ range [°]	3.898–49.52
Reflections collected	13551
Independent reflections, *Rint*	3319, 0.0551
Data /restraints /parameters	3319/145/399
Final $R1$ values ($I >= 2\sigma(I)$)	0.1555
Final $R1$ values (all data)	0.4375
Final $wR(F_2)$ values (all data)	0.5004
Goodness-of-fit on F^2	1.146
Largest difference peak and hole [e.A-3]	0.61 /-0.46
The number of observed reflections	1873
CCDC	2279795

Crystals of **EtP5⊃TTF** were prepared via a vapor diffusion method. First, 1.00 mg of **TTF** and 6.00 mg of **EtP5** were dissolved in 1 mL of dioxane. Subsequently, the mixture was added to a small bottle and the bottle was then placed in a covered beaker containing 2 mL of methanol as the poor solvent. Methanol gradually diffused into the solution of **TTF** and **EtP5**. After 2 days, a large number of **EtP5⊃TTF** crystals were obtained.

Notes: **TTF** exhibited a significant disorder in this crystal structure.

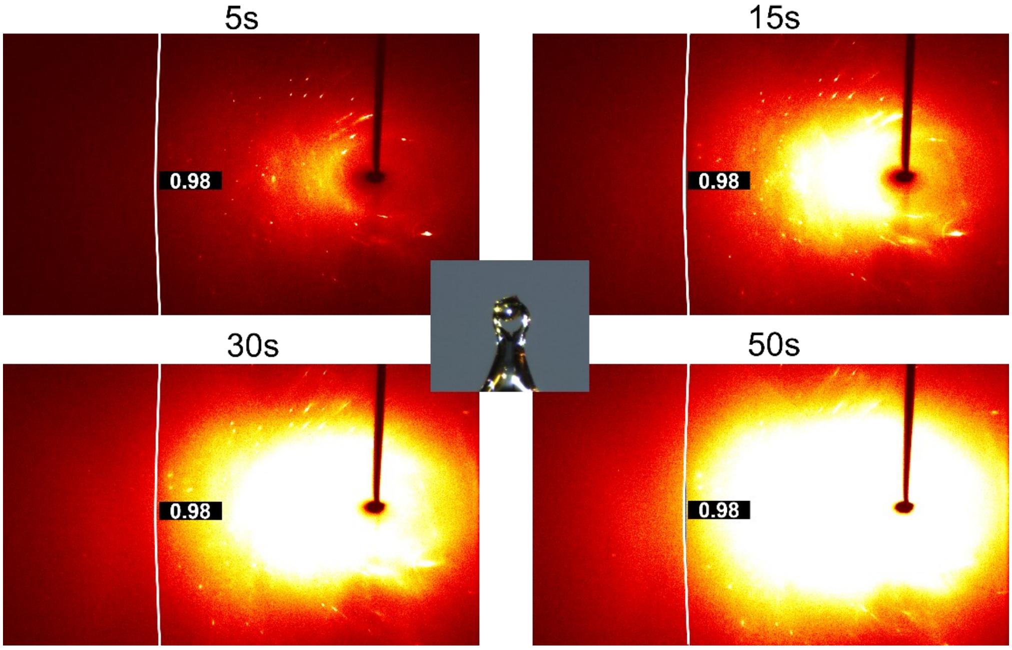

Figure S6. Images of frames with exposure time of 5s, 15s, 30s and 50s, showing no obvious improvement of the resolution above 0.98 Å.

To obtain a higher quality of this crystal data, elongation the exposure time from 5s to 15s, 30s and 50s were tried (Figure S6). However, the images below didn't show obvious improvement of the resolution above 0.98 Å. The current crystal data is the best that we can obtain.

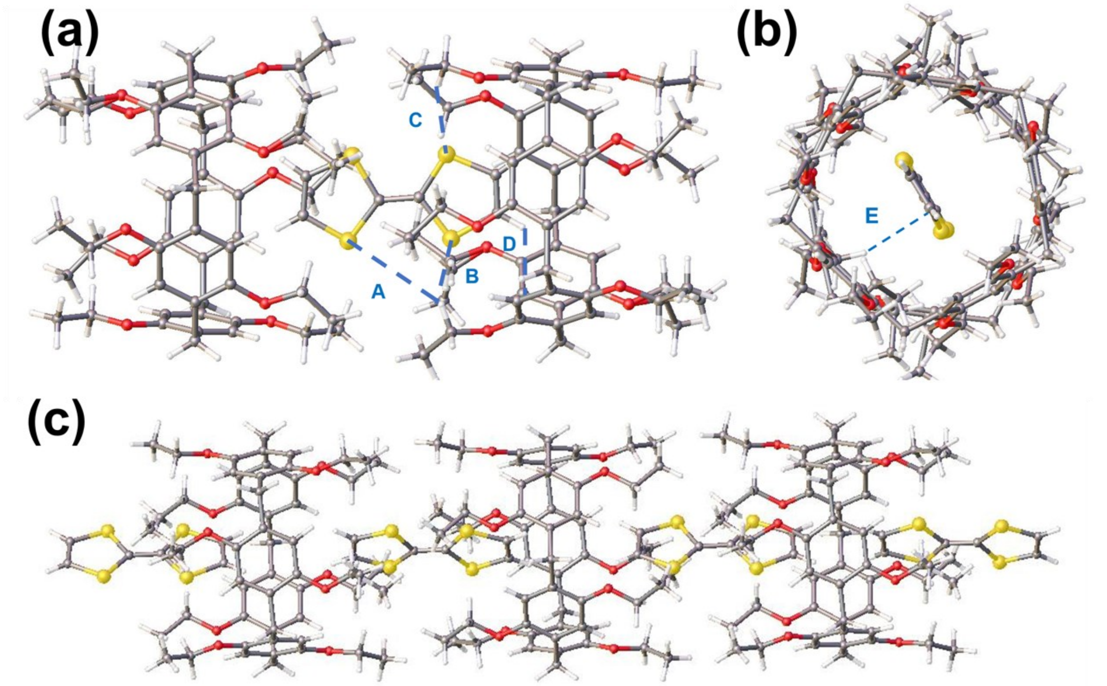

Figure S7. (a–c) Different views of the crystal structure of **EtP5⊃TTF**. For **EtP5**, carbon atoms are grey, oxygen atoms are red, and hydrogen atoms are white. For **TTF**, carbon atoms are grey, sulfur atoms are yellow, and hydrogen atoms are white. C−H···S interaction parameters: C–H···S distances (Å): **A**: 2.96; **B**: 2.67; **C**: 2.83. C−H···π interaction parameters: C−H···π distances (Å): **D**: 3.02; **E**: 2.91.

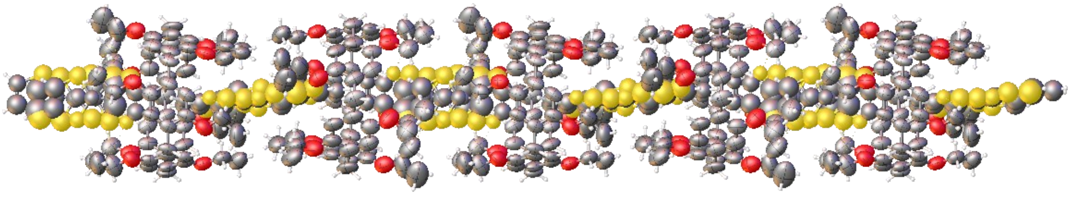

Figure S8. Ellipsoids structure of the host−guest complex between **EtP5** and **TTF**, with 50% probability thermal ellipsoids.

In the crystal data, C27 and C28 atoms exhibited a positional disorder over two positions. The two orientations were separated using PART 1 and PART 2 instructions and refined using a free variable (FVAR). DFIX, SADI instructions were used to fix the disordered parts in reasonable shape and positions. SIMU (0.02 0.04 esds) instructions were used to make the anisotropic displacement parameters of the disordered parts within reasonable limits. In the final refinement, the occupancies of 0.602:0.398 have been determined for PART 1 and PART 2 of the disordered C27 and C28 atoms. Meanwhile, PART -1 and PART -2 instructions were used in the refinement of **TTF** since the molecule disordered across the inversion center. The occupancy of each part was fixed to 0.25 and refined as isotropic.

*5. The crystal structure of **TTF***

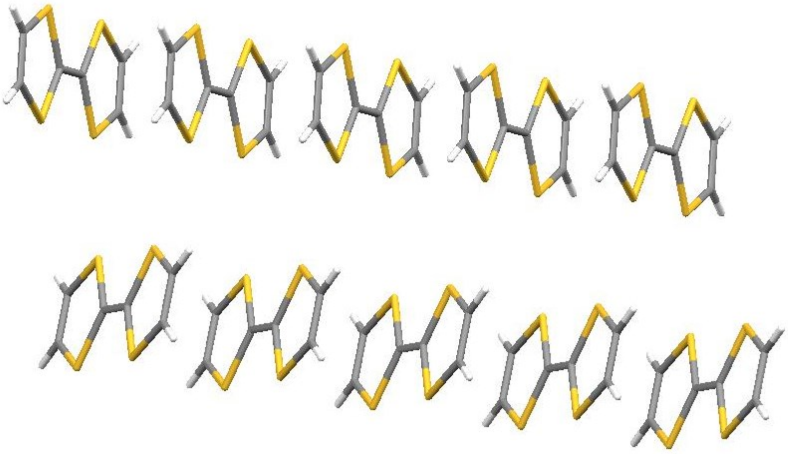

Figure S9. The crystal structures of **TTF**. CCDC number 618631.

*6. The crystal structure of **EtP5***

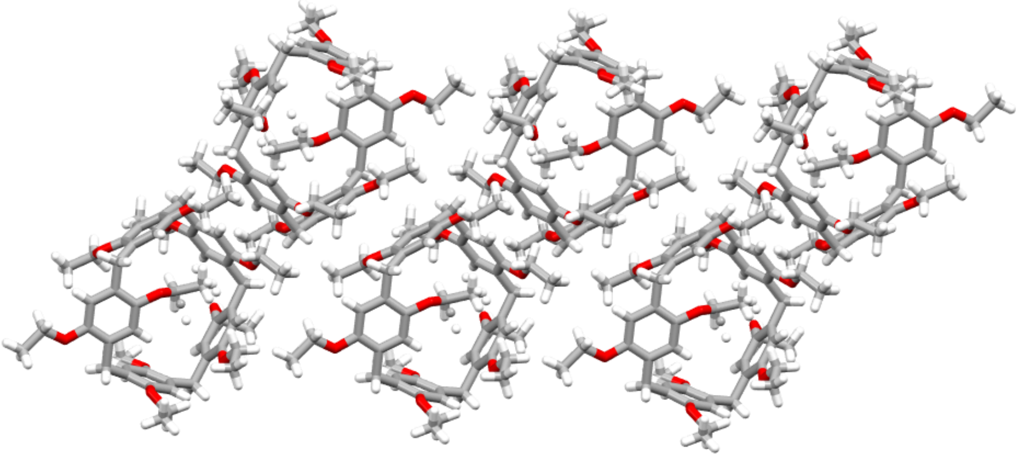

Figure S10. The crystal structures of **EtP5**. CCDC number 1817584.

*7. ^{1}H NMR spectrum of the crystal of **EtP5** and **TTF***

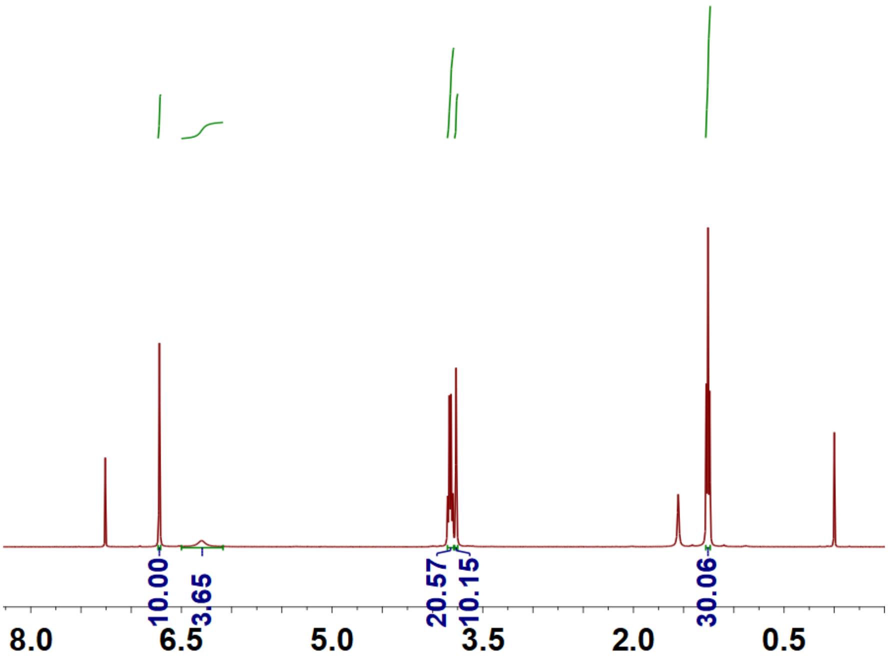

Figure S11. The ^{1}H NMR of the cocrystal **EtP5⊃TTF**.

8. References

S1. K. Jie, Y. Zhou, E. Li, R. Zhao, M. Liu, F. Huang, *J. Am. Chem. Soc.*, 2018, **140**, 3190−3193.

S2 W. Xia, X.-Y. Hu, Y. Chen, C. Lin, L. Wang, *Chem. Commun.* 2013**, 49**, 5085−5087.