Supporting Information for

Macrocyclic Diacetylene-Terthiophene Cocrystal: Molecular Self-Assembly, Topochemical Polymerization and Energy Transfer

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1. Crystallographic data for MCDA-needle, MCDA-plate, and MCDA-3T.

Table S1. Crystallographic data for **MCDA-Needle**, **MCDA-plate**, and **MCDA-3T**.

	MCDA-needle	**MCDA-plate**	**MCDA-3T**
Empirical formula	C_{44} H_{52} O_8	$C_{44}H_{52}O_8$	C_{44} H_{52} O_8
Formula weight	708.85	708.85	708.85
Temperature (K)	293(2)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P 2_1/c	P 1 2_1/c 1	P -1
a (Å)	4.7766(2)	21.1848(5)	4.7070(6)
b (Å)	41.0190(13)	9.0139(2)	12.6273(16)
c (Å)	12.2047(4)	10.3103(2)	22.195(3)
α (º)	90.00	90	100.8467(14)
β (º)	94.6748(17)	95.3959(13)	91.3126(14)
γ (º)	90.00	90	92.9553(14)
Volume (Å ^{3})	2383.33(15)	1960.11(7)	1293.2(3)
Z	2	2	1
Density (calc.) (Mg/m^3)	0.988	1.201	0.910
Absorption coefficient (mm^{-1})	0.067	0.081	0.062
Crystal size (mm^3)	0.10 x 0.30 x 0.35	0.20 x 0.36 x 0.40	0.20 x 0.17 x 0.06
Reflections collected	57567	60949	41840
Independent reflections	4012 [R(int) = 0.0379]	4877 [R(int) = 0.0692]	6572 [R(int) = 0.0617]
Data / restraints /parameters	4012 / 0 / 235	4877 / 0 / 237	6572 / 0 / 236
Goodness-of-fit on F^2	1.093	1.068	1.027
Final R indices [I>2σ (I)]	R_1 = 0.1100, wR_2 = 0.2433	R_1 = 0.0566, wR_2 = 0.1394	R_1 = 0.0668, wR_2 = 0.1390
R indices (all data)	R_1 = 0.1218,	R_1 = 0.0930,	R_1 = 0.1319,

Table S2. Bond distances for **MCDA-Needle**, **MCDA-plate**, and **MCDA-3T**.

	MCDA-needle	**MCDA-plate**	**MCDA-3T**
C–C(Å)	1.355(5)-1.515(5)	1.379(3)-1.527(3)	1.383(2)-1.524(3)
C≡C(Å)	1.186(6), 1.196(6)	1.194(3), 1.169(3)	1.182(3), 1.198(3)
C–O(Å)	1.315(5)-1.443(6)	1.367(2)-1.427(2)	1.337(3)-1.452(3)
C=O(Å)	1.253(8), 1.261(8)	1.203(2)	1.200(3)

Table S3. Geometric Parameters for **MCDA-Needle**, **MCDA-plate**, and **MCDA-3T**

Type of crystal	**d_1 (Å)**	**d_2 (Å)**	**α (°)**	**Interior cavity (Å ^{2})**	**Exterior cavity (Å ^{2})**
MCDA-needle	4.78	4.11	56.0	8.27 x 14.85	-
MCDA-plate	10.31	8.12	45.4	6.49 x 17.11	-
MCDA-3T	4.71	4.11	56.8	8.65 x 14.79	7.74 x 9.30

2. Photophysical data for 3T and MCDA-3T.

Table S4. Photophysical data for **3T** and **MCDA-3T**

	λ_{max}^{abs} (nm)	λ_{max}^{em} (nm)	Φ_{FL} (%)	τ_{FL} (ns)
3T solution[1]	354	407 426	6.6	0.21
3T film[2]	320 410	450 480	2	0.083
MCDA-3T	-	436 465 487 (sh)	3.3	0.49

sh = Shoulder, λ_{max}^{abs} = Maximum absorption wavelength, λ_{max}^{em} = Maximum emission wavelength, Φ_{FL} = Fluorescence quantum yield τ_{FL} = Fluorescence lifetime

3. Optical microscopic images for MCDA crystals and MCDA-3T cocrystals.

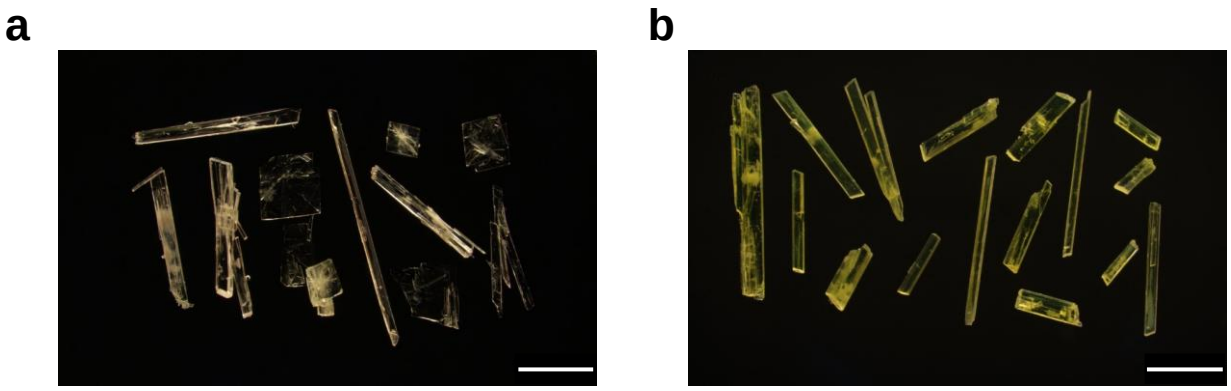

Figure S1. Optical microscopic images of **MCDA** crystals yielding **MCDA-needle** and **MCDA-plate** crystals (a) and **MCDA-3T** cocrystals (b). Crystals were obtained from slow evaporation of tetrahydrofuran solutions. Scale bar: 500 μm.

4. Crystal structures of MCDA-plate

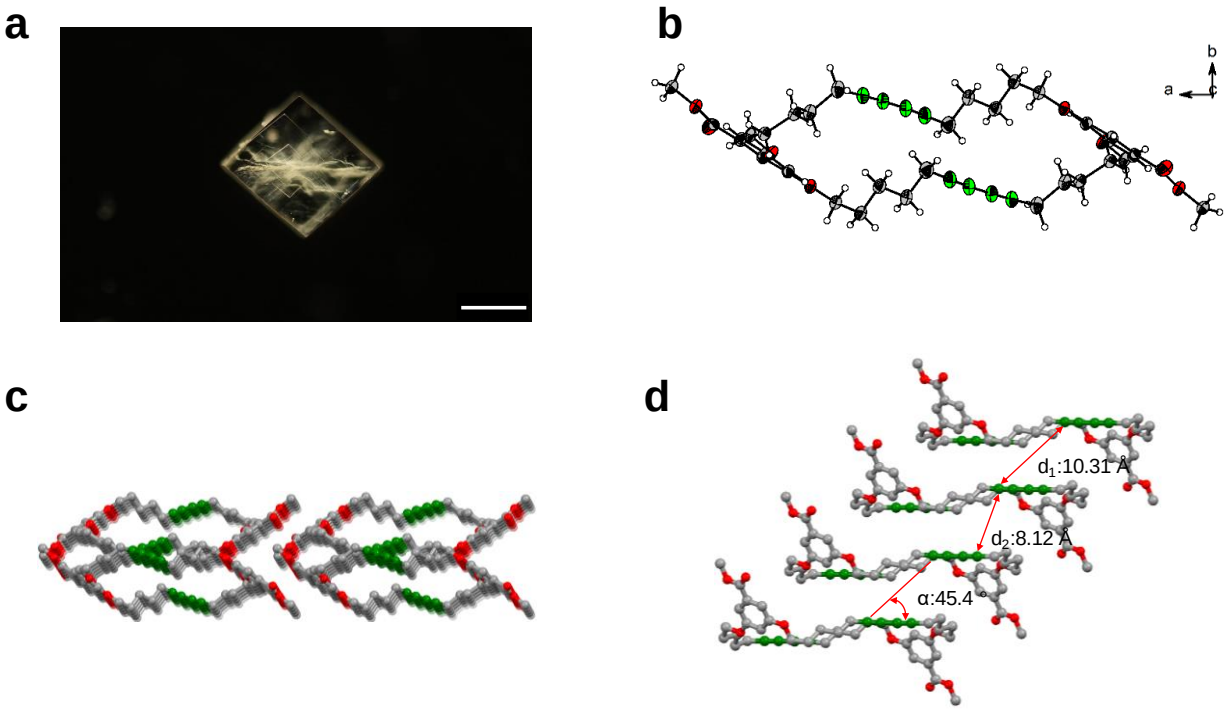

Figure S2. Crystal structure of **MCDA-plate.** (a) Magnified optical microscopic image of **MCDA-plate**. (b) Ellipsoid diagram showing the crystal structure with split type inner-cavity. (c) View along the column axis of crystal structures. MCDA stacked in Zigzag fashion. (b) Side view of four consecutive MCDAs. The MCDA units adopt a chairlike conformation.

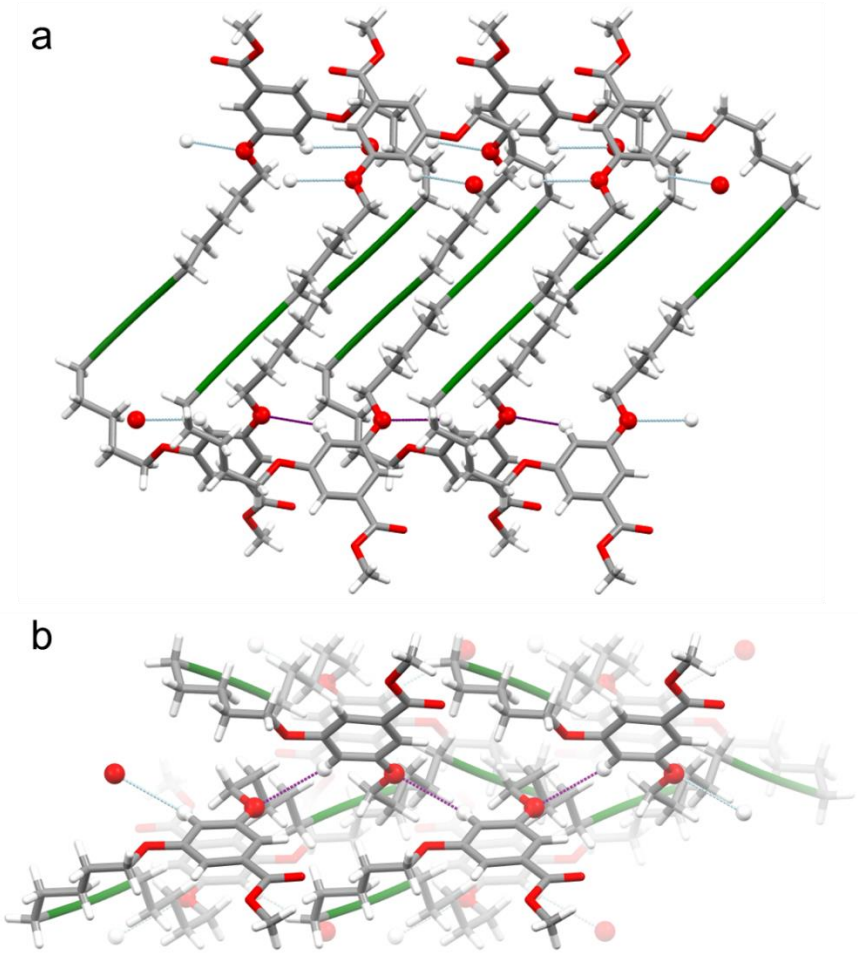

Figure S3. Intermolecular hydrogen bonds in **MCDA-plate** crystal. Hydrogen bonds between aromatic C–H and ether O are indicated with violet and pale blue dashed line in (a) side view and (b) front view.

5. ORTEP drawings for MCDA-needle, MCDA-plate, and MCDA-3T

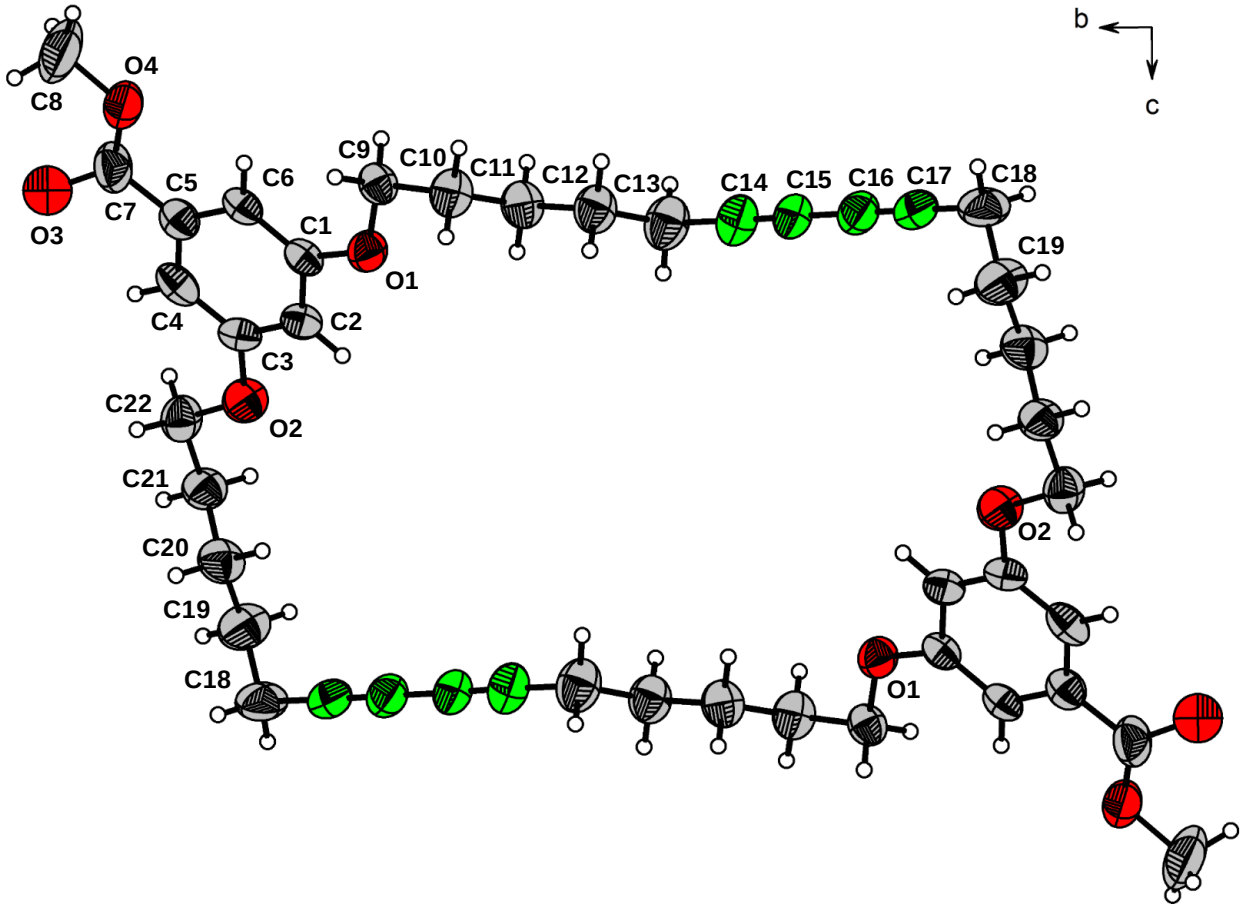

Figure S4. ORTEP diagram of **MCDA-needle** with atomic labeling.

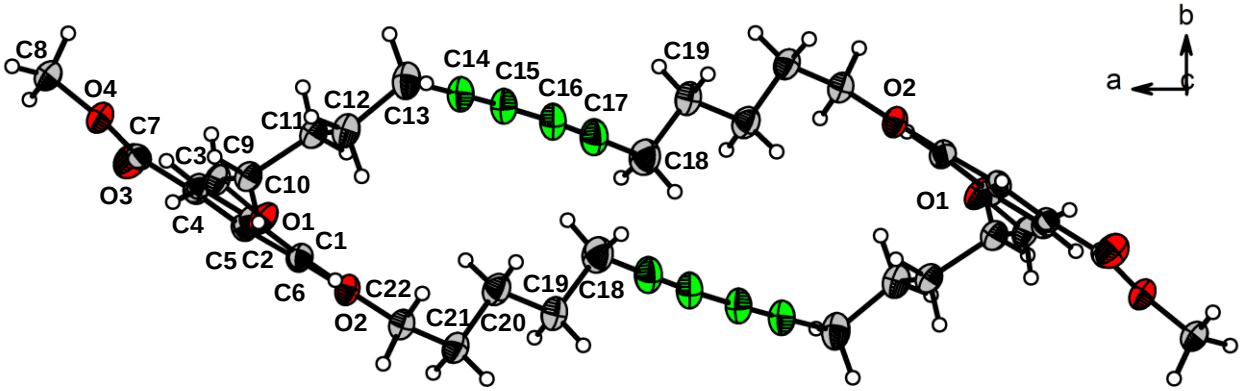

Figure S5. ORTEP diagram of **MCDA-plate** with atomic labeling.

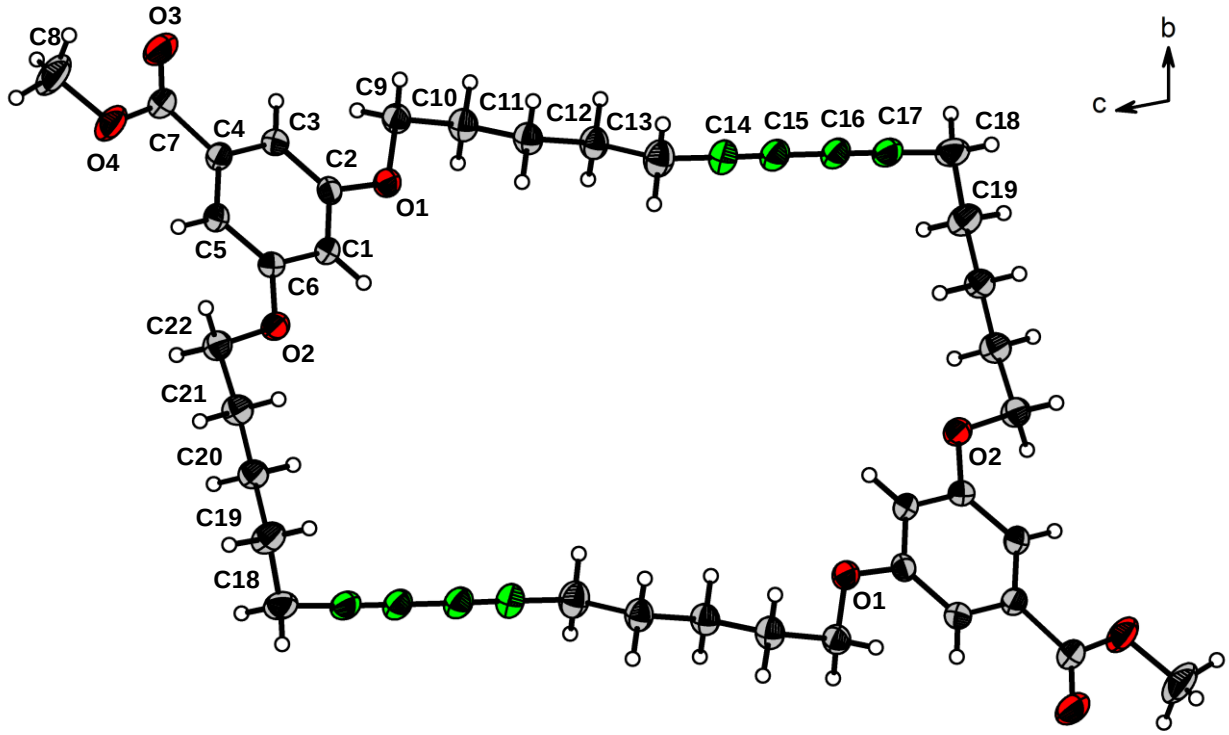

Figure S6. ORTEP diagram of **MCDA-3T** with atomic labeling.

6. ^{1}H NMR spectra for MCDA-3T inclusion cocrystal.

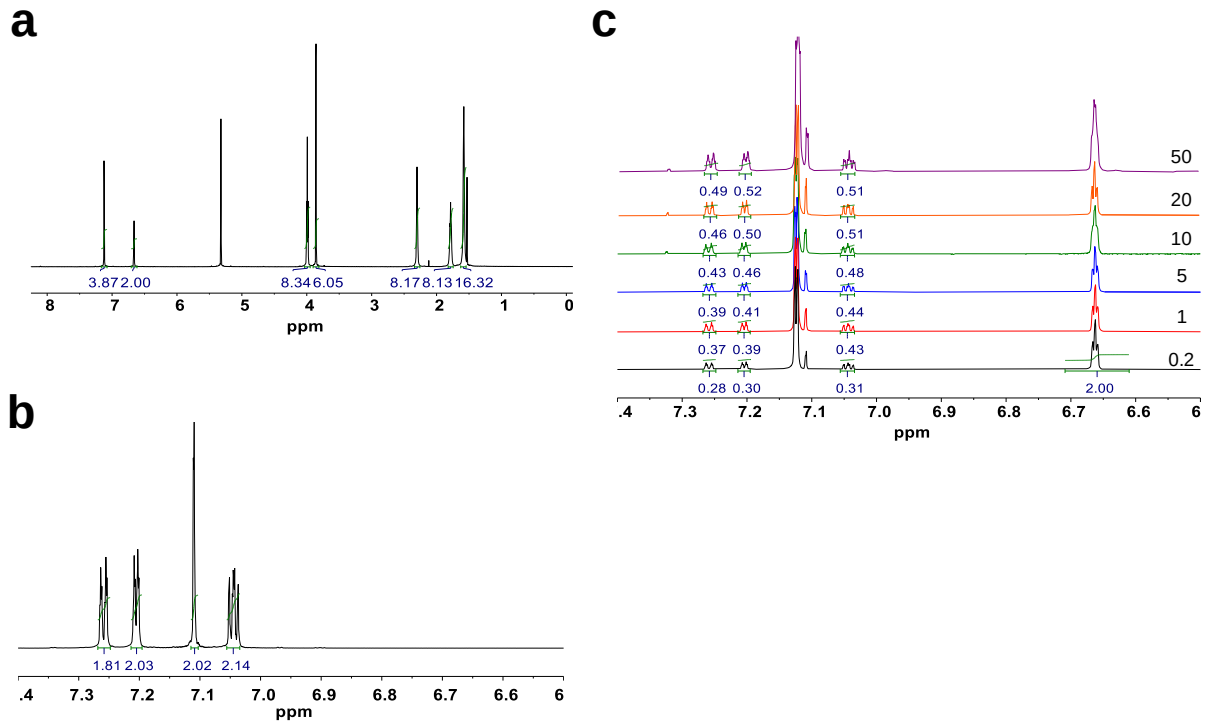

Figure S7. MCDA-3T inclusion cocrystal. ^{1}H NMR spectra in methylene chloride-d_2: **MCDA** (a), **3T** (b), and **MCDA-3T** cocrystal (c) with varying the molar ratio of **3T** to **MCDA**.

7. Polarized fluorescence microscopic images of the MCDA-3T cocrystal.

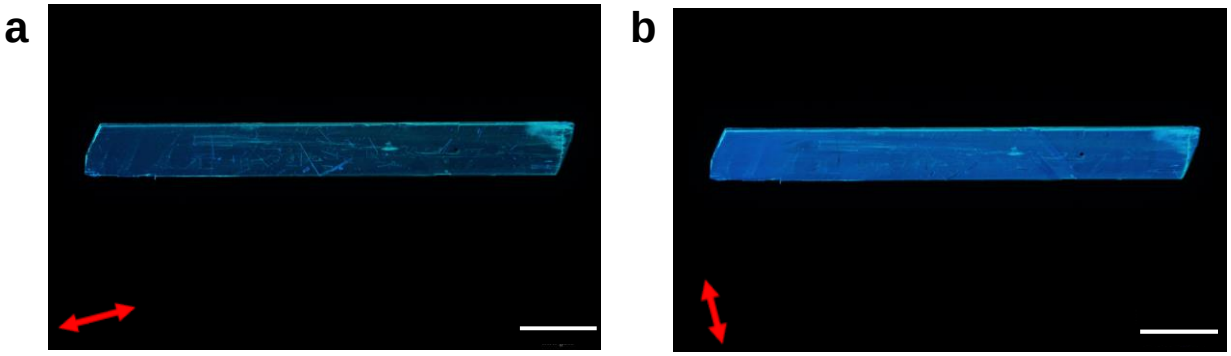

Figure S8. Polarized fluorescence microscopic images of the **MCDA-3T** cocrystal. The arrows indicate the direction of the analyzer axis. Scale bar: 500 μm.

8. Topochemical polymerization of MCDA-needle.

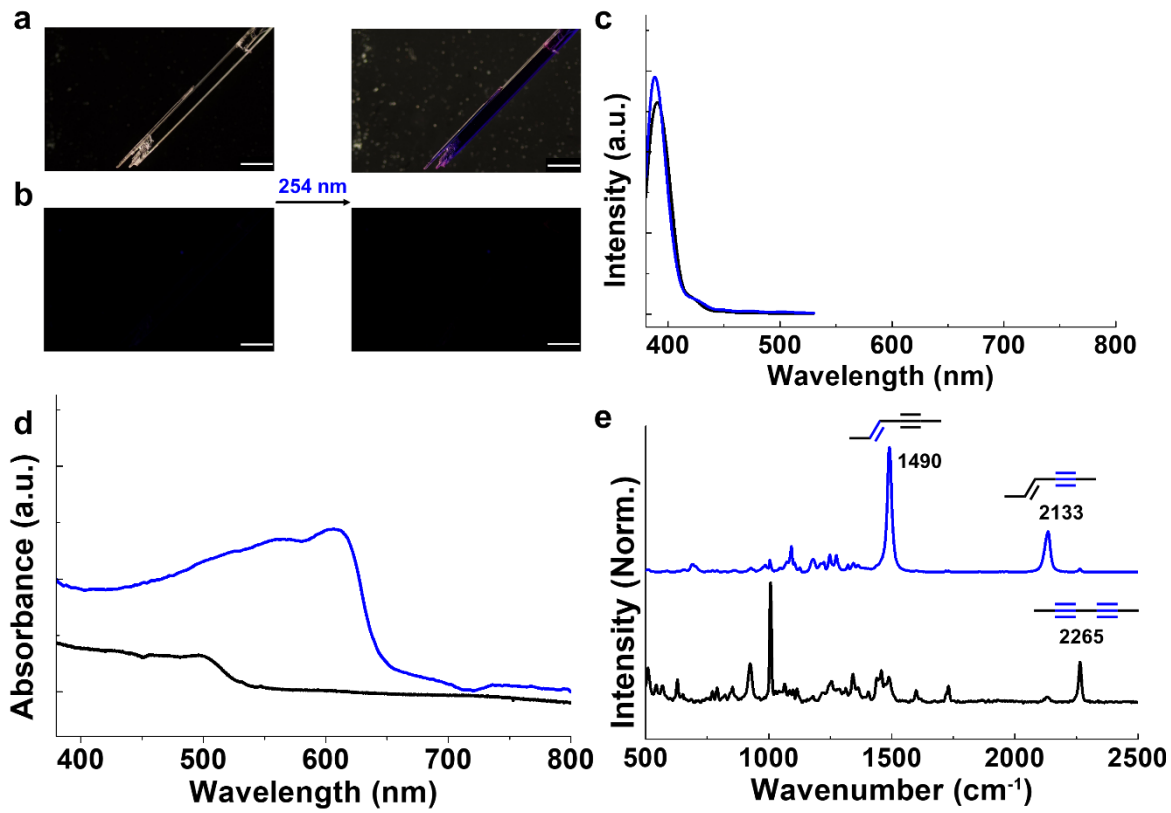

Figure S9. Topochemical polymerization of **MCDA-needle**. Optical (a) and fluorescence (b) microscopic images of a monomer **MCDA-needle** crystal before (left) and after (right) 254 nm UV irradiation (25 mW/cm^2) for 5 min (scale bar: 500 μm). Fluorescence (c), UV-vis absorption (d) and Raman spectra (e) of **MCDA-needle** before (black color) and after (blue color) 254 nm UV irradiation (25 mW/cm^2) for 5 min. Fluorescence spectrum was recorded at the excitation wavelength of 375 nm.

9. Fluorescence emission and UV-vis absorption spectra of MCDA and 3T.

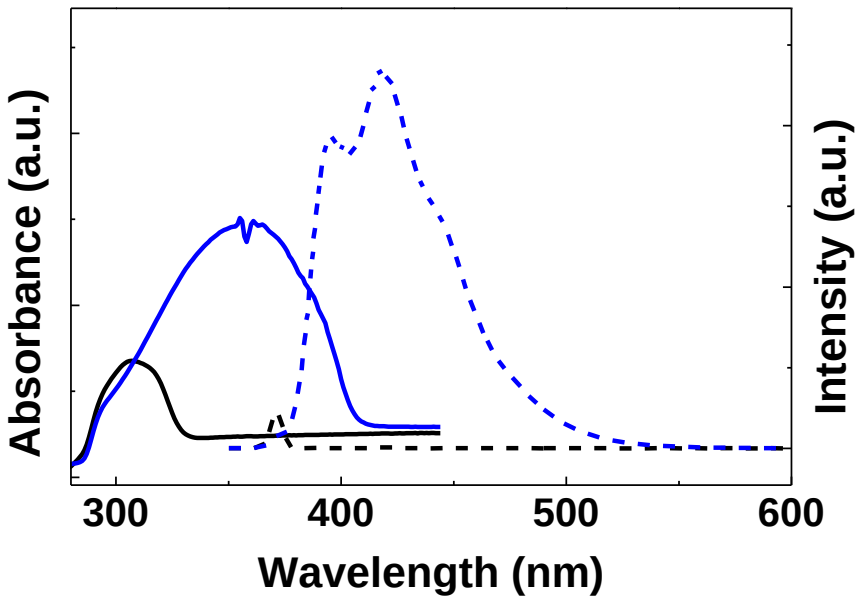

Figure S10. Fluorescence emission and UV-vis absorption spectra of **MCDA** and **3T**. Fluorescence emission (dashed) and UV-vis absorption (solid) of THF solution of **MCDA** (black: 0.04mM) and **3T** (blue: 0.04 mM).

References

1. Becker, R. S.; Demelo, J. S.; Macanita, A. L.; Elisei, F. Comprehensive Investigation of the Solution Photophysics and Theoretical Aspects of Oligothiophenes of 1-7 Rings. *Pure Appl. Chem.* **1995,** 67, 9-16.

2. Moreau, J.; Giovanella, U.; Bombenger, J. P.; Porzio, W.; Vohra, V.; Spadacini, L.; Di Silvestro, G.; Barba, L.; Arrighetti, G.; Destri, S.; Pasini, M.; Saba, M.; Quochi, F.; Mura, A.; Bongiovanni, G.; Fiorini, M.; Uslenghi, M.; Botta, C. Highly emissive nanostructured thin films of organic host-guests for energy conversion. *ChemPhysChem* **2009,** 10, 647-653.