Electronic Supplementary Material (ESI) for CrystEngComm.

Head-to-tail photodimerization of a thiophene in a co-crystal and a rare adipic acid dimer in the presence of a heterosynthon

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Supplementary Information Content:

1) Experimental information

Unless otherwise noted, all starting materials and solvents were commercially available from Aldrich Chemical Co.

β-PTE was synthesized as previously reported.[1]

Preparation of co-crystals: Co-crystals were obtained by dissolving **β-PTE** (15 mg, 0.08 mmol) and the appropriate dicarboxylic acid (0.04 mmol) in an organic solvent (succinic acid(**SA**): tetrahydrofuran, glutaric acid(**GA**): acetonitrile, adipic acid(**AA**): ethyl acetate). All solutions were filtered through a cotton plug. The solutions were allowed to evaporate slowly over 1-2d. The obtained co-crystals were colorless and displayed plate- or prism-shaped morphologies.

UV-irradiation experiments: Finely ground samples of 2(**β-PTE**)·(**SA**), 2(**β-PTE**)·(**GA**), and (**β-PTE**)·(**AA**) (30 mg) were irradiated using a 500 W broadband mercury lamp. The progress of the photoreaction was monitored by ^{1}H NMR spectroscopy.

Separation of photoproduct from CCF: The photoirradiated powder of 2(**β-PTE**)·(**SA**) was stirred in a 1M solution of potassium hydroxide for 15 minutes under low heat. The photoproduct was extracted from the solution with dichloromethane, dried with $MgSO_4$, and the solvent was removed. The powder was redissolved in a solution of 3:2 CH_3CN:toluene (*v*/*v*). Slow solvent evaporation over 3 days yielded colorless plate-shaped crystals suitable for single crystal X-ray diffraction.

2) ^{1}H NMR Spectroscopy

^{1}H NMR data was collected on an AVANCE Bruker NMR spectrometer operating at 300 MHz using DMSO-d_6 as the solvent.

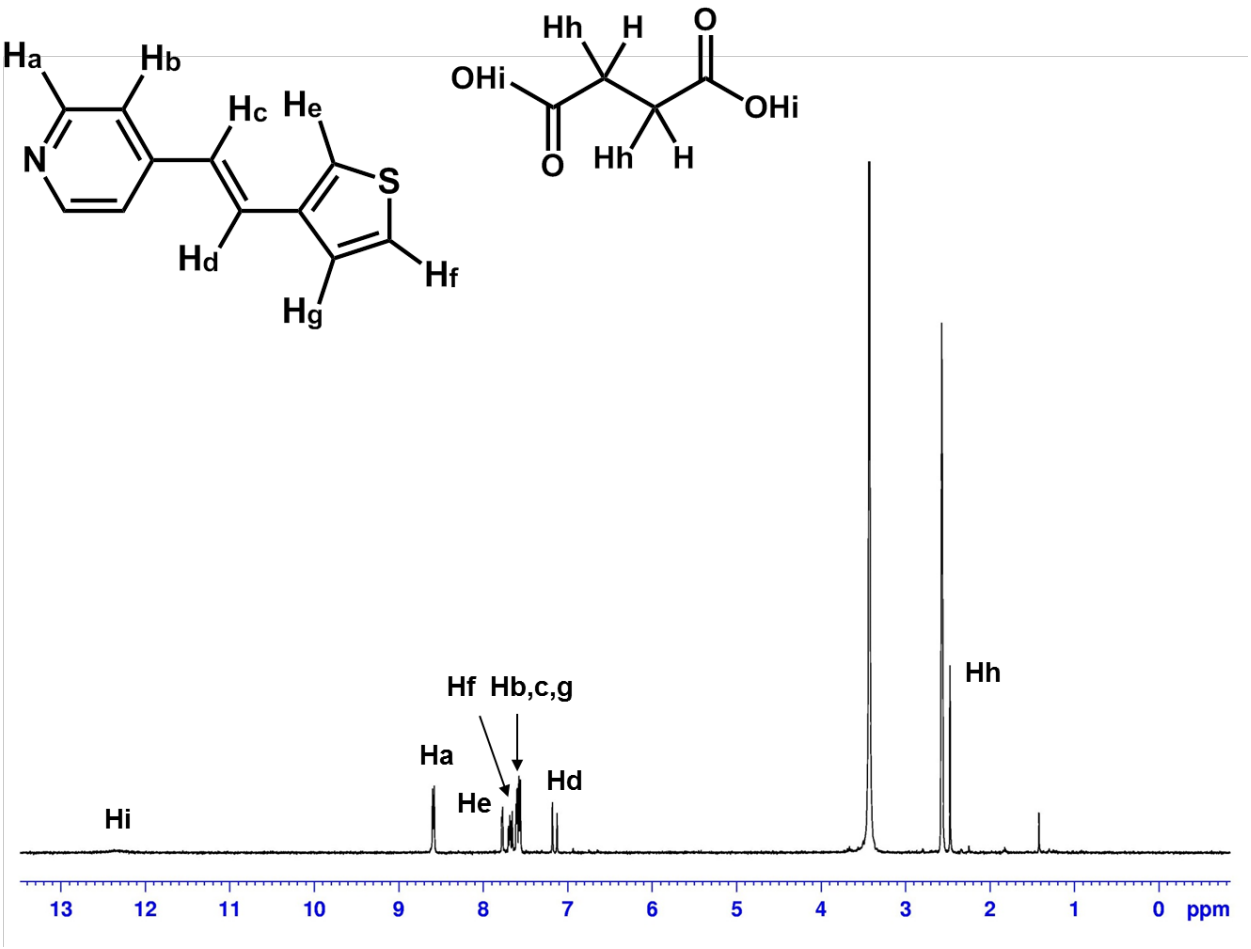

Figure S1. Spectrum of 2(**β-PTE**)·(**SA**).

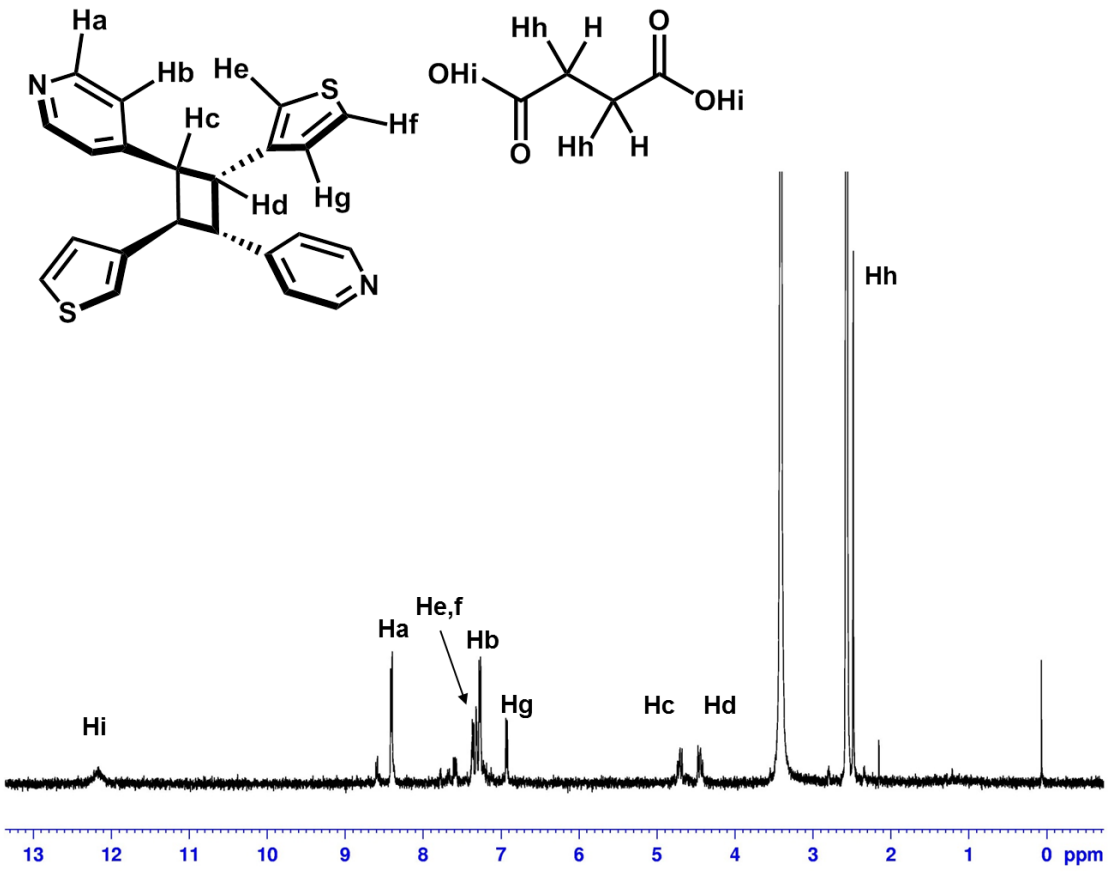

Figure S2. Spectrum of 2(**β-PTE**)·(**SA**) after 110 hrs UV irradiation.

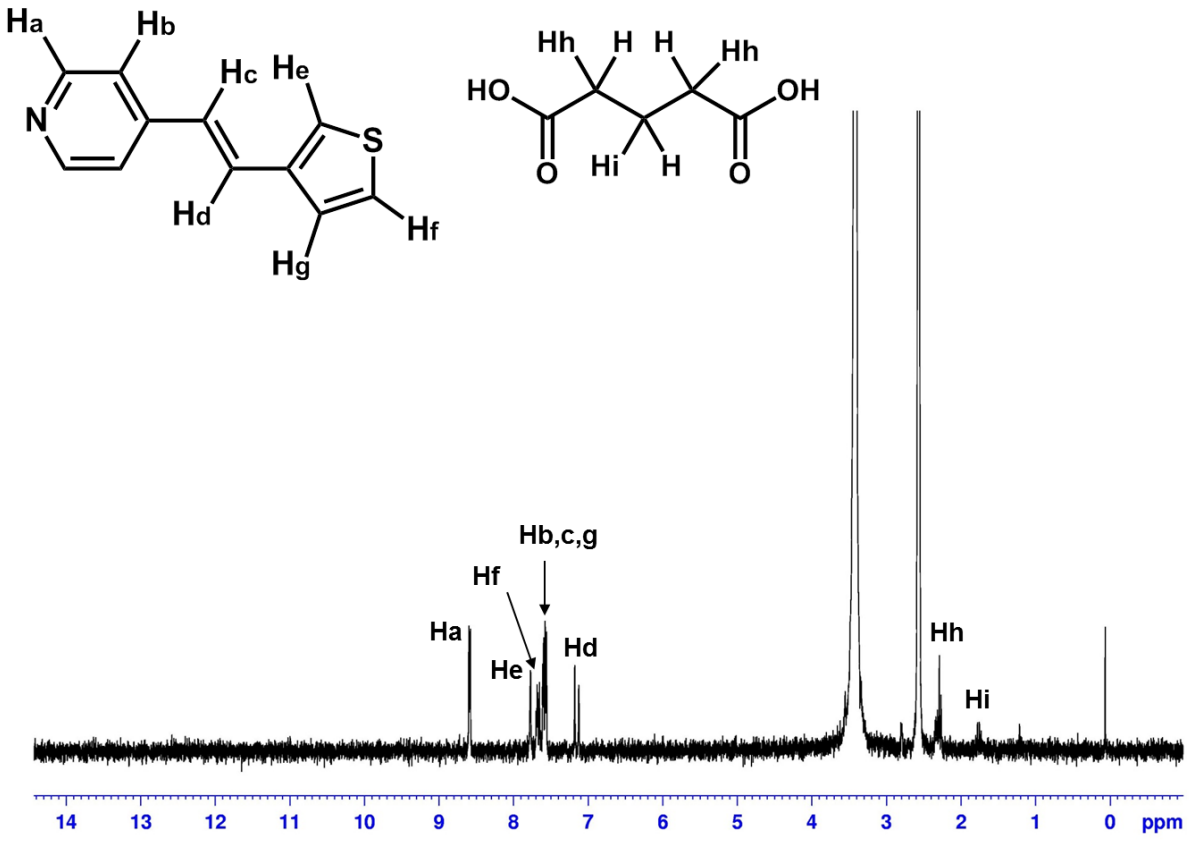

Figure S3. Spectrum of 2(**β-PTE**)·(**GA**).

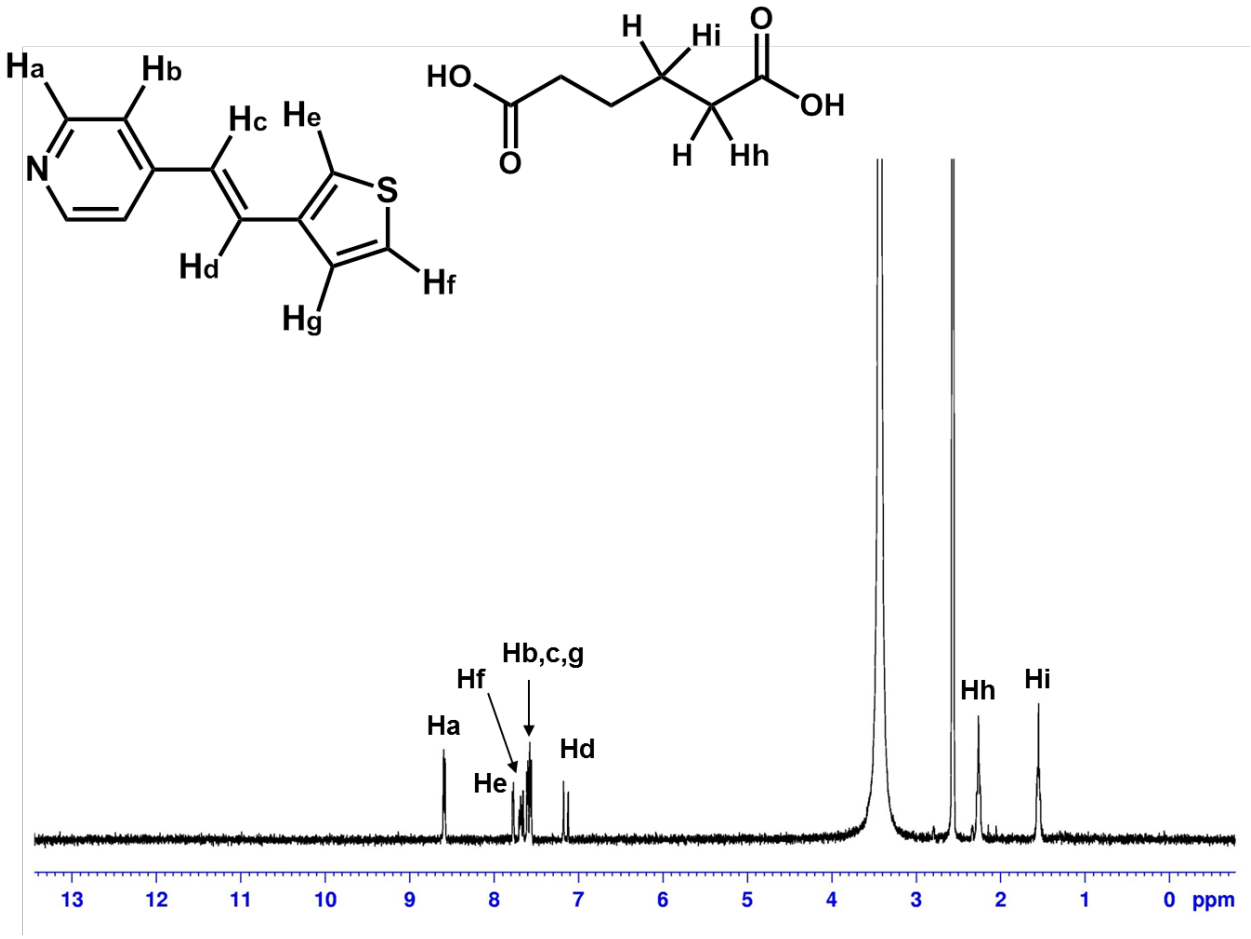

Figure S4. Spectrum of (**β-PTE**)·(**AA**).

3) Single crystal X-ray diffraction

Single-crystal XRD was measured on a Nonius Kappa CCD single-crystal X-ray diffractometer using MoK_α radiation (λ =0.7107 Å). Structure solution and refinement were accomplished using SHELXS-97 and SHELXL-97, respectively.[2] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms associated with carbon atoms were refined in geometrically constrained positions.

Table S1. Crystallographic parameters for 2(**β-PTE**)·(**SA**) and **4p3tc**.

compound name	**2(β-PTE)·(succinic acid)**	**4p3tc**
chemical formula	$2(C_{11}H_9NS)\cdot C_4H_6O_4$	$C_{22}H_{18}N_2S_2$
formula mass	492.59	374.5
crystal system	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$
a/Å	9.283(1)	11.689(1)
b/Å	19.692(2)	15.176(2)
c/Å	13.665(2)	12.166(1)
α/°	90	90
β/°	108.704(5)	117.334(5)
γ/°	90	90
V/Å^3	2365.9(4)	1917.1(3)
ρ_{calc} /g cm^{-3}	1.383	1.298
T/K	298(2)	298(2)
Z	4	4
radiation type	MoK_α	MoK_α
μ /mm^{-1}	0.262	0.285
no. of reflections measured	15445	10820
no. of independent reflections	4156	3380
no of reflection (I > 2σ(I))	2713	2218
R_{int}	0.0645	0.0354
R_1 (I > 2σ(I))	0.0591	0.0443
$wR(F^2)$ (I > 2σ(I))	0.1319	0.1052
R_1 (all data)	0.1029	0.0822
$wR(F^2)$ (all data)	0.1523	0.1268
CCDC deposition number	989758	989759

Table S2. Crystallographic parameters for 2(**β-PTE**)·(**GA**) and (**β-PTE**)·(**AA**).

compound name	**2(β-PTE)·(glutaric acid)**	**(β-PTE)·(adipic acid)**
chemical formula	$2(C_{11}H_9NS)\cdot C_5H_8O_4$	$C_{11}H_9NS\cdot C_6H_{10}O_4$
formula mass	506.61	333.39
crystal system	monoclinic	triclinic
space group	$P2_1/c$	P-1
a/Å	15.935(2)	5.6534(6)
b/Å	7.3782(7)	8.1587(8)
c/Å	21.823(3)	18.996(2)
α/°	90	83.851(5)
β/°	100.382(5)	83.879(5)
γ/°	90	74.142(5)
V/Å^3	2523.8(5)	835.2(2)
ρ_{calc} /g cm^{-3}	1.333	1.326
T/K	190(2)	298(2)
Z	4	2
radiation type	MoK_α	MoK_α
μ /mm^{-1}	0.247	0.213
no. of reflections measured	43736	3741
no. of independent reflections	4433	2472
no of reflection (I > 2σ(I))	3525	1190
R_{int}	0.0318	0.0601
R_1 (I > 2σ(I))	0.0408	0.061
$wR(F^2)$ (I > 2σ(I))	0.096	0.1012
R_1 (all data)	0.0564	0.1643
$wR(F^2)$ (all data)	0.1041	0.1279
CCDC deposition number	989760	989761

References

1) K. M. Hutchins, J. C. Sumrak and L. R. MacGillivray, *Org. Lett*., **2014**, *16*, 1052.
2) G. M. Sheldrick, *Acta Crystallogr. A*, **2008**, *64*, 112.