Electronic Supplementary Material (ESI) for ChemComm.

Superstructural diversity in salt-cocrystals: higher-order hydrogen-bonded assemblies formed using U-shaped dications and with assistance of π^{-}-π stacking

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Supporting Information (SI)

S1: Synthesis

Iocoumarin-3-acid,[1] DPN,[2] and DEPN[3] were synthesized according to the literature. All solvents were purchased from Sigma-Aldrich and used as received.

Synthesis of 1,8-bis[(4-pyridyl)acetylene]naphthalene (DAPN):

4-Ethynylpyridine was synthesized following procedure reported in literature.[4] Diisopropylamine (10 ml) was degassed under N_2 atmosphere at room temperature for 30 min. To a mixture of 1,8-diiodonapthalene (1 mmol), Pd[$(PPh3)_2Cl_2$] (0.015 mmol), and CuI (0.015 mmol) a degassed diisopropylamine was transferred using cannula. After stirring for 30 mins 4-ethynylpyridine (3 mmol) was added and the mixture was heated at 70 °C for 48 hours. For work up: solvent was removed under vacuum and water was added to remaining residue. Resulting aqueous solution was extracted 3 times with dichloromethane. Combined organic layers were dried over Na_2SO_4. Solvent was removed in vacuo to give crude product which was purified by column chromatography using hexane-ethyl acetate as eluent. ^{1}H NMR (300 MHz): δ 8.38-8.40 (4H, d, J=6 Hz, PyH), 8.14-8.17 (2H, d, J= 9 Hz, Napth-H), 7.97-8.00 (2H, d, J = 9 Hz, Napth-H), 7.63-7.68 (2H, t, Napth-H); 7.28-7.30 (4H, d, J=6 Hz, PyH).

Synthesis of salt co-crystals:

a. Synthesis of [**DEPN-2H**][**Iso**]$_2$·2(**IsoH**) (**1**)

1 was obtained mechanochemically by kneading (with mortar and pestle) Isocoumarin (50 mg, 0.26 mmol) and DEPN (22.0 mg, 0.066 mmol) in 4:1 ratio for 20 minutes in the presence of nitromethane (2 drops).

Single crystals: Pale yellow parallelepiped-like single crystals of **1** were obtained by slow evaporation of mixed nitromethane/methanol (v:v 4:1) solutions of isocoumarin-3-acid (25.0 mg, 0.13 mmol) and DEPN (11.0 mg, 0.03 mmol) (4:1 ratio) over the period of 3 days.

b. [DAPN-2H][Iso]$_2$·2(IsoH) (2)

2 was obtained mechanochemically by kneading (with mortar and pestle) Isocoumarin (50 mg, 0.26 mmol) and DAPN (21. mg, 0.066 mmol) in 4:1 ratio for 20 minutes in the presence of nitromethane (2 drops).

Single crystals: Mixing methanol solutions (3 ml each) of isocoumarin-3-acid (25.0 mg, 0.13 mmol) and DAPN (10.9 mg, XX mmol) (4:1 molar ratio) on slow evaporation gave pale orange plate-like single crystals of **2** ($DAPNH^+$·$2Iso^-$·2IsoH) after 1 day.

c. [**DPN-2H][Iso]**$_2$·2(**IsoH**)·3**NO$_2$Me** (**3**)

3 was obtained mechanochemically by kneading (with mortar and pestle) Isocoumarin (50 mg, 0.26 mmol) and DPN (18.6 mg, 0.066 mmol) in 4:1 ratio for 20 minutes in the presence of nitromethane (2 drops).

Single crystals: Mixing nitromethane/ethanol (v:v 4:1) solutions (3 ml each) of isocoumarin-3-acid (25.0 mg, 0.13 mmol) and DPN (9.28 mg, 0.03 mmol) (4:1 ratio) on slow evaporation gave colorless prisms of **3** after 1 day.

S2: ^{1}H NMR Spectral Data

^{1}H NMR spectra were collected using a *Bruker* 300 MHz spectrometer and using **DMSO**-*d6* as a solvent. All data were processed with MestReNova suite of software programs.

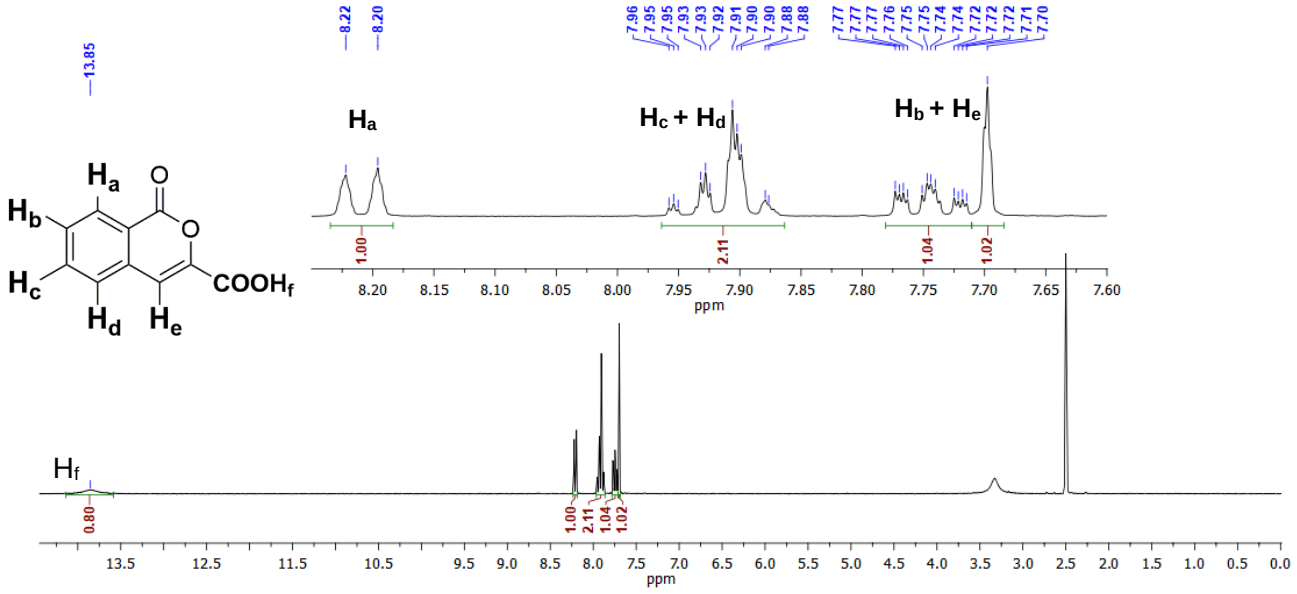

Figure S1. ^{1}H NMR spectrum of **IsoH** in **DMSO-*d6***.

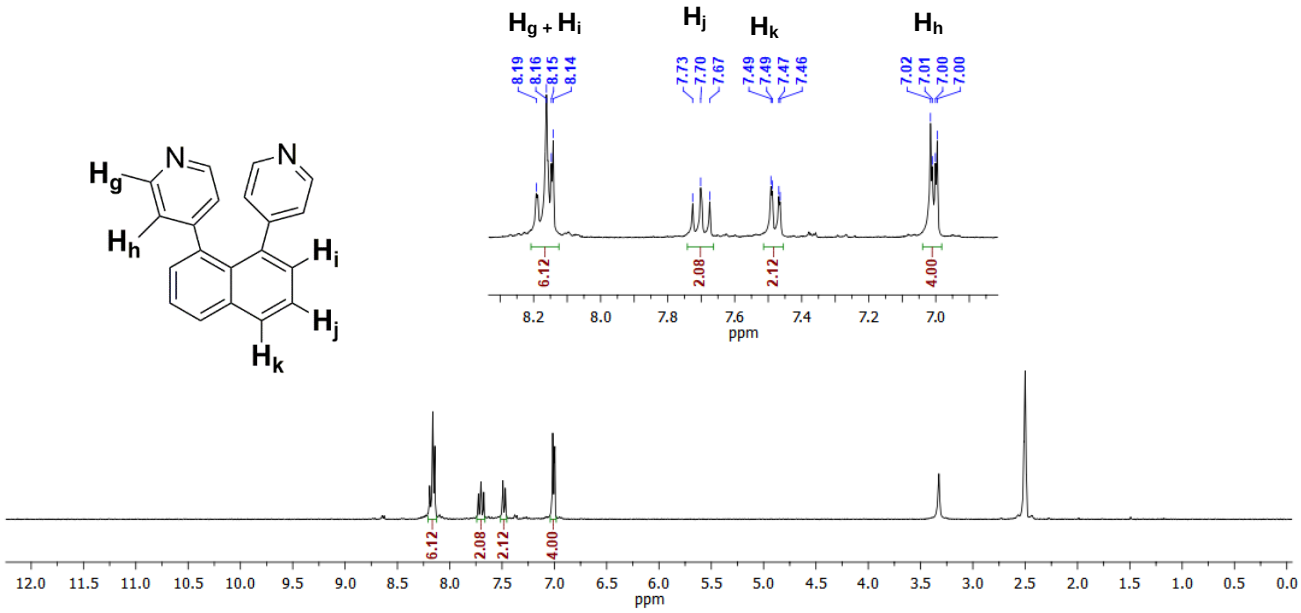

Figure S2. ^{1}H NMR spectrum of **DPN** in **DMSO-*d6***.

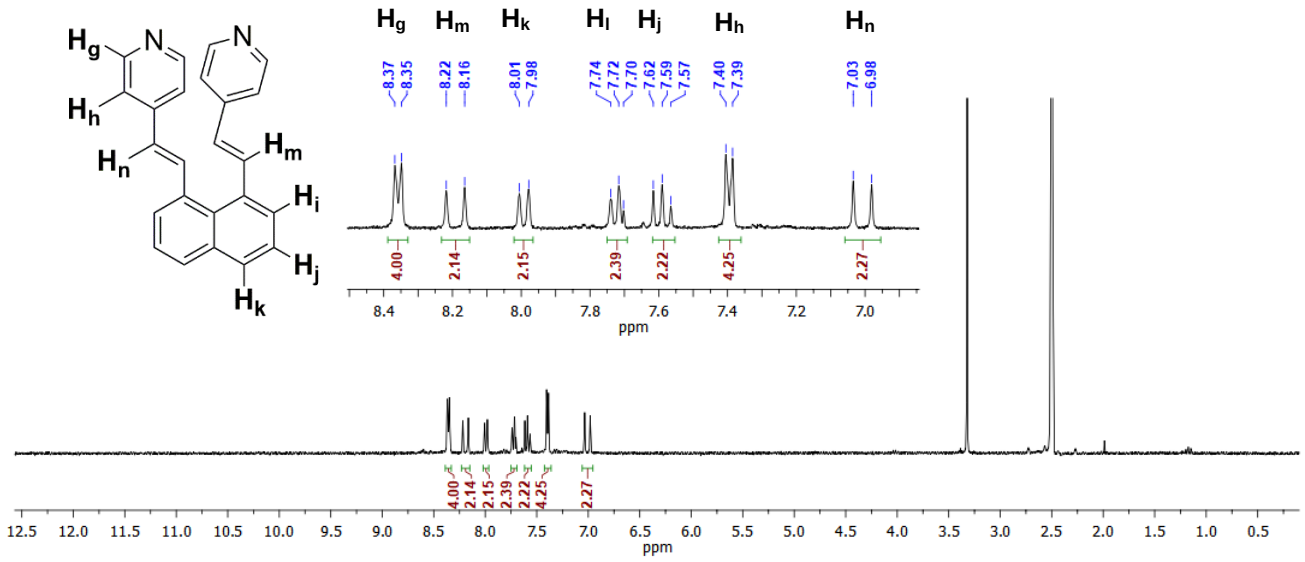

Figure S3. ^{1}H NMR spectrum of **DEPN** in **DMSO-*d6***.

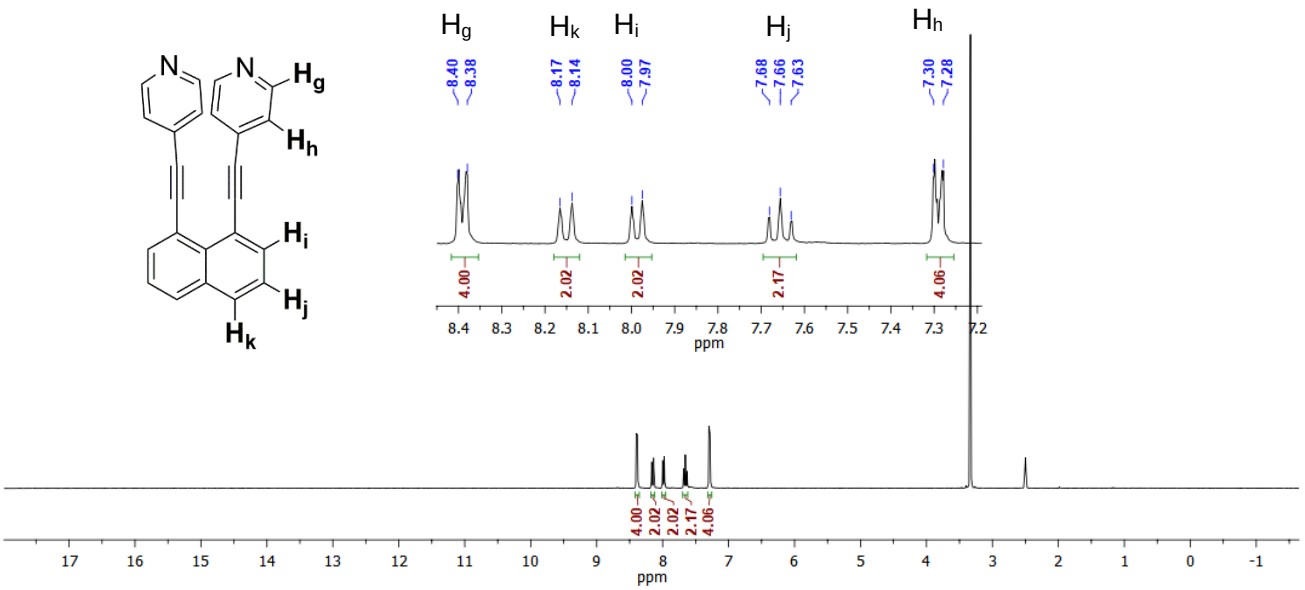

Figure S4. ^{1}H NMR spectrum of **DAPN** in **DMSO-*d6***.

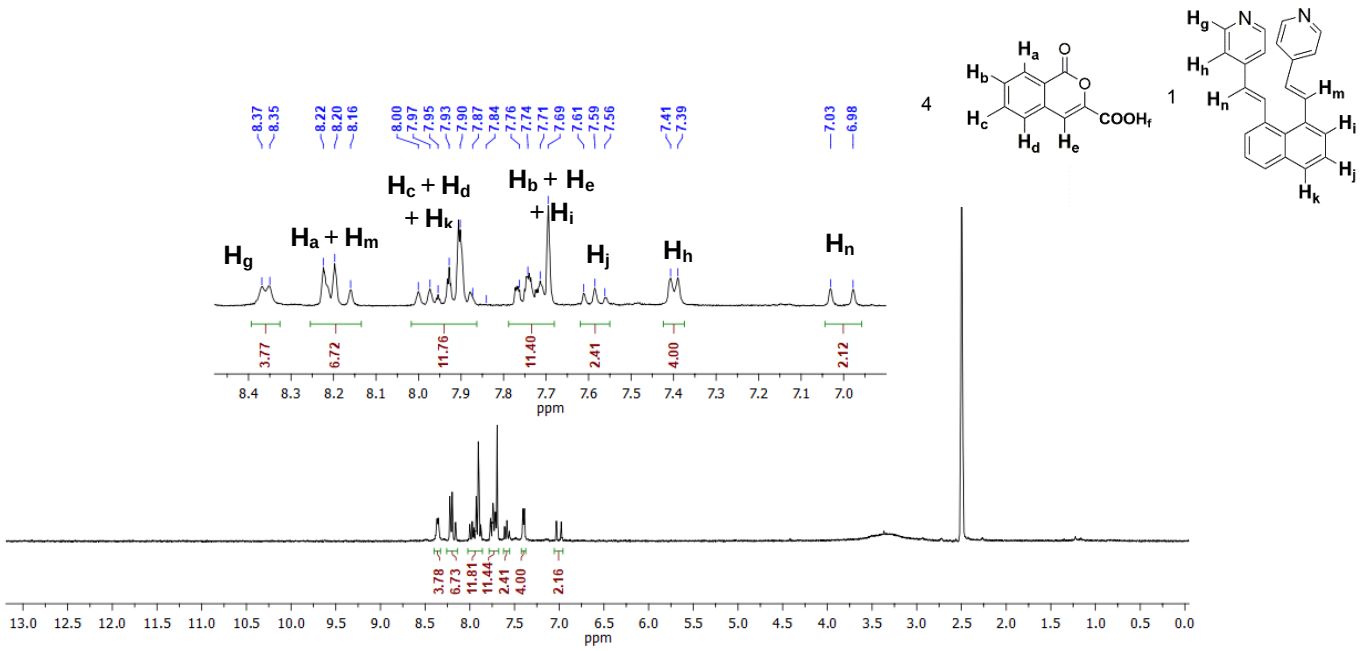

Figure S5. ^{1}H NMR spectrum of **2** in **DMSO-*d6*.**

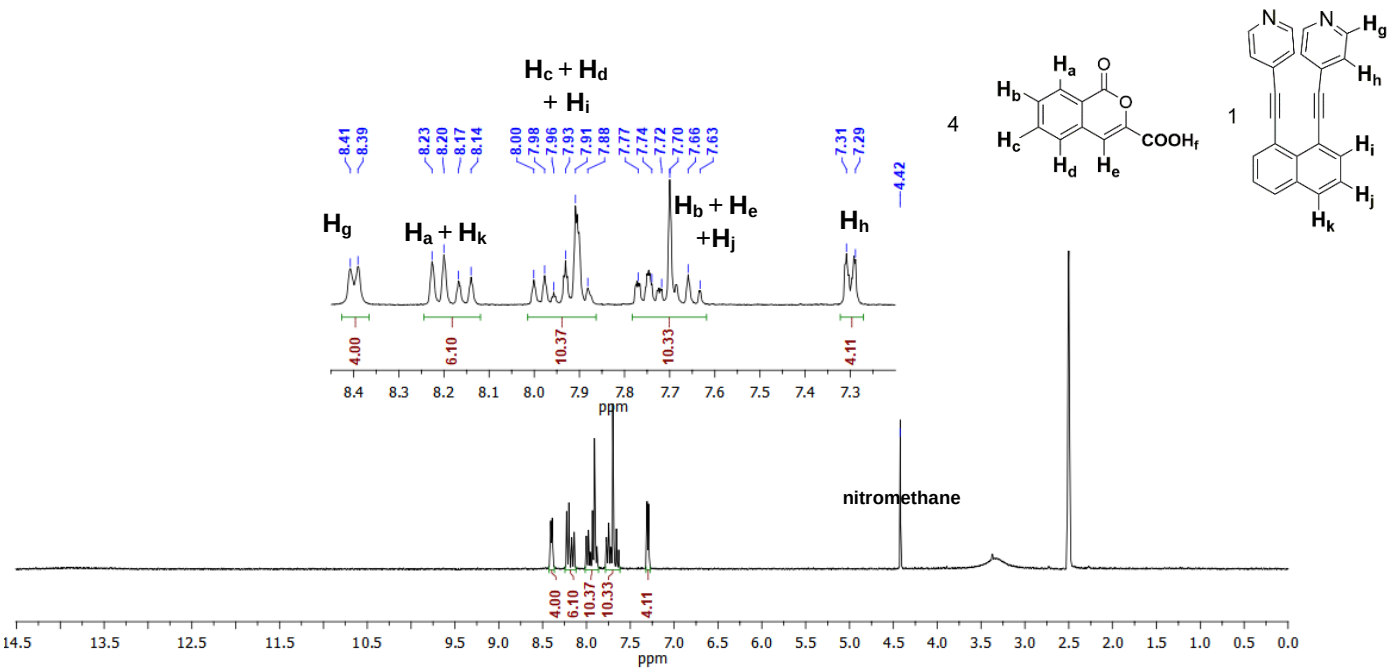

Figure S6. ^{1}H NMR spectrum of **2** in **DMSO-*d6*.**

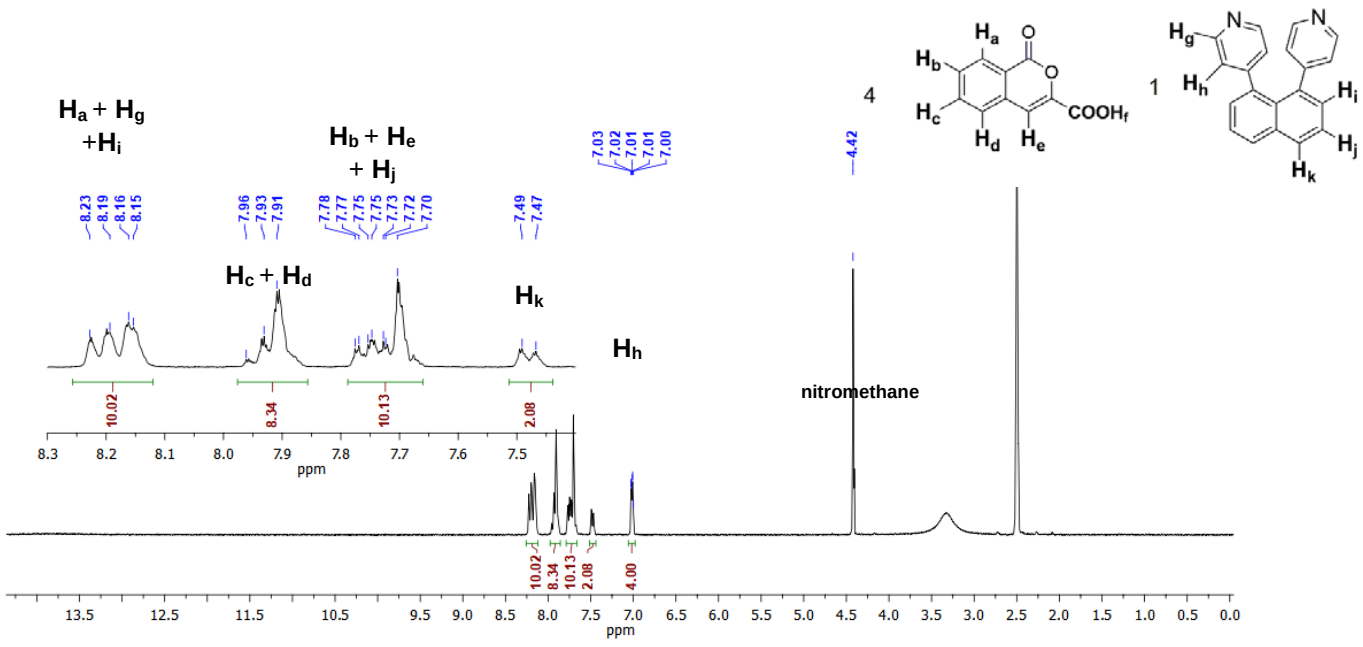

Figure S7. ^{1}H NMR spectrum of **3** in **DMSO-*d6*.**

S3: Powder X-ray Diffraction Data

PXRD data were collected from samples mounted on glass slides by a Bruker D8 Advance X-ray diffractometer using CuKα radiation (λ = 1.54056 Å) (scan type: locked coupled; scan mode: continuous; step size: 0.02°). Note: SCXRD of **1**, **2**, and **3** is collected at low temperature.

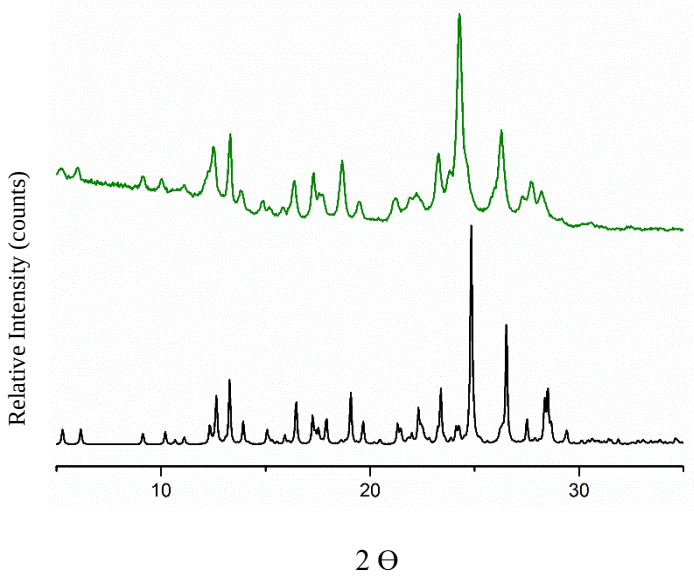

Figure S8. Powder X-ray diffraction comparison of **1** obtained by kneading experiment (top) with simulated pattern from single crystal X-ray diffraction data.

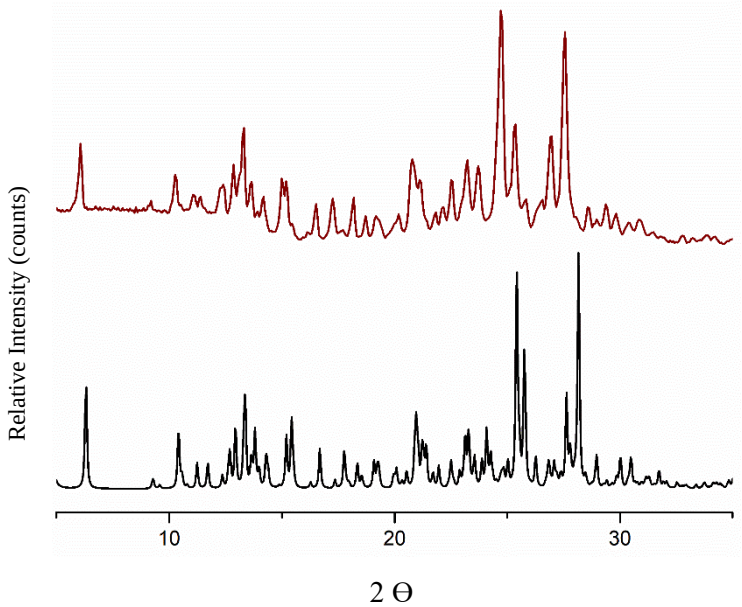

Figure S9. Powder X-ray diffraction comparison of **2** obtained by kneading experiment (top) with simulated pattern from single crystal X-ray diffraction data.

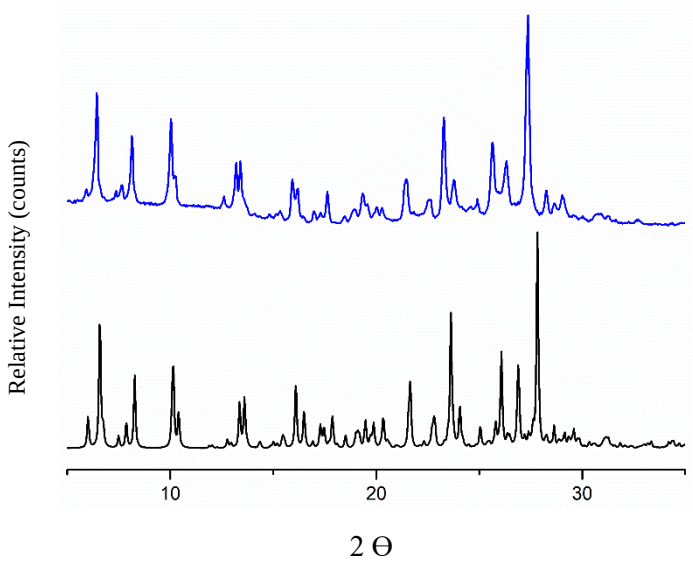

Figure S10. Powder X-ray diffraction comparison of **1** obtained by kneading experiment (top) with simulated pattern from single crystal X-ray diffraction data.

S4: Single-Crystal X-ray Diffraction Data

X-ray data were collected on either Nonius Kappa CCD or Nonius APEX II Kappa diffractometer at room temperature using MoKa radiation (λ = 0.71073 Å). Structure solution and refinement were accomplished using Olex2,[5] SHELXT[6] and SHELXL.[7] All nonhydrogen atoms were identified from the difference Fourier map within several refinement steps. Hydrogen atoms associated with carbon atoms were refined in geometrically constrained positions with isotropic thermal parameter.

Crystal Data for **1** (CCDC 1906138) $C_{64}H_{42}N_2O_{16}$ (M =1094.99 g/mol): monoclinic, space group $P2_1/c$, a = 8.4167(5) Å, b = 28.6453(15) Å, c = 20.8697(12) Å, β = 100.155(5)°, V = 4952.8(5) Å^3, Z = 4, T = 100.02 K, μ(CuKα) = 0.888 mm^{-1}, *Dcalc* = 1.468 g/cm^3, 60014 reflections measured (5.294° ≤ 2Θ ≤ 136.482°), 9044 unique (R_{int} = 0.0846). The final R_1 was 0.0589 and wR_2 was 0.1752 (all data).

Crystal Data for **2** (CCDC 1906139) $C_{64}H_{38}N_2O_{16}$ (M =1090.96 g/mol): triclinic, space group $P\bar{1}$, a = 8.8579(9) Å, b = 15.7231(16) Å, c = 20.017(2) Å, α = 110.471(5)°, β = 93.635(5)°, γ = 106.238(5)°, V = 2467.0(4) Å^3, Z = 2, T = 150.15 K, μ(MoKα) = 0.107 mm^{-1}, *Dcalc* = 1.469 g/cm^3, 38303 reflections measured (4.416° ≤ 2Θ ≤ 52.934°), 10085 unique (R_{int} = 0.0558). The final R_1 was 0.0524 and wR_2 was 0.1325 (all data).

Crystal Data for **3** (CCDC 1906137) $C_{63}H_{47}N_5O_{22}$ (M =1226.05 g/mol): triclinic, space group $P\bar{1}$, a = 13.7033(14) Å, b = 14.2585(14) Å, c = 15.6635(16) Å, α = 104.701(5)°, β = 100.957(5)°, γ = 99.729(5)°, V = 2829.3(5) Å^3, Z = 2, T = 190.15 K, μ(MoKα) = 0.111 mm^{-1}, *Dcalc* = 1.439 g/cm^3, 20617 reflections measured (4.636° ≤ 2Θ ≤ 52.066°), 11116 unique (R_{int} = 0.0197). The final R_1 was 0.0513 and wR_2 was 0.1532 (all data).

Table S1: Crystal data and structure refinement for **1.**

CCDC	1906138
Empirical formula	$C_{64}H_{42}N_2O_{16}$
Formula weight	1094.99
Temperature/K	100.02
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.4167(5)
b/Å	28.6453(15)
c/Å	20.8697(12)
α/°	90
β/°	100.155(5)
γ/°	90
Volume/Å^3	4952.8(5)
Z	4
ρ_{calc}g/cm^3	1.468
μ/mm^{-1}	0.888
F(000)	2272.0
Crystal size/mm^3	0.129 × 0.071 × 0.039
Radiation	CuKα (λ = 1.54178)
Reflections collected	60014
Independent reflections	9044 [R_{int} = 0.0846, R_{sigma} = 0.0543]
Final R indexes [I>=2σ (I)]	R_1 = 0.0589, wR_2 = 0.1595
Final R indexes [all data]	R_1 = 0.0790, wR_2 = 0.1752

Table S2: Crystal data and structure refinement for **2.**

CCDC	1906139
Empirical formula	$C_{64}H_{38}N_2O_{16}$
Formula weight	1090.96
Temperature/K	150.15
Crystal system	triclinic
Space group	P-1
a/Å	8.8579(9)
b/Å	15.7231(16)
c/Å	20.017(2)
α/°	110.471(5)
β/°	93.635(5)
γ/°	106.238(5)
Volume/Å^3	2467.0(4)
Z	2
ρ_{calc}g/cm^3	1.469
μ/mm^{-1}	0.107
F(000)	1128.0
Crystal size/mm^3	0.13 × 0.12 × 0.03
Radiation	MoKα (λ = 0.71073)
Reflections collected	38303
Independent reflections	10085 [R_{int} = 0.0558, R_{sigma} = 0.0793]
Final R indexes [I>=2σ (I)]	R_1 = 0.0524, wR_2 = 0.1112
Final R indexes [all data]	R_1 = 0.1144, wR_2 = 0.1325

Table S3: Crystal data and structure refinement for **3.**

CCDC	1906137
Identification code	mcg1711
Empirical formula	$C_{63}H_{47}N_5O_{22}$
Formula weight	1226.05
Temperature/K	190.15
Crystal system	triclinic
Space group	P-1
a/Å	13.7033(14)
b/Å	14.2585(14)
c/Å	15.6635(16)
α/°	104.701(5)
β/°	100.957(5)
γ/°	99.729(5)
Volume/Å^3	2829.3(5)
Z	2
ρ_{calc}g/cm^3	1.439
μ/mm^{-1}	0.111
F(000)	1272.0
Crystal size/mm^3	0.38 × 0.24 × 0.18
Radiation	MoKα (λ = 0.71073)
Reflections collected	20617
Independent reflections	11116 [R_{int} = 0.0197, R_{sigma} = 0.0336]
Final R indexes [I>=2σ (I)]	R_1 = 0.0513, wR_2 = 0.1353
Final R indexes [all data]	R_1 = 0.0779, wR_2 = 0.1532

Table S5. The C-O bond parameter 1-2.

Salt cocrystal	anionic Iso^- (Assembly) [C−O^-] Å	neutral IsoH (Assembly) [C−O] Å	anionic Iso^- (lattice) [C−O^-] Å	neutral IsoH (Lattice) [C−O] Å
1	1.240(4)/1.276(4)	1.231(3)/ 1.281(4)	1.230(3)/1.273(3)	1.221(3)/1.294(3)
2	1.242(3)/1.272(3)	1.234(3)/1.284(3)	1.231(3)/1.273(3)	1.217(3)/1.306(3)

Table S6 . The C-O bond parameter 3.

Salt cocrystal	anionic Iso^- (Assembly) [C−O^-] Å		neutral IsoH (Assembly) [C−O] Å	
3	1.258(3)/1.246(2)	1.232(2)/1.264(3)	1.217(2)/1.293(2)	1.215(2)/1.302(3)

S5: Theoretical calculations

The calculations have been performed by using the program Gaussian'09 revision D01.[8] The structural optimizations energies of all complexes included in this study were computed at the B97-D3/6-31G(d) level of theory.[9] All minima were verified using frequency calculations. No symmetry constraints were used during the optimization. The superfine grid was used in the DFT optimization of all complexes. Single point energies were calculated using B97-D3/def2-TZVP level of theory. We have used methanol as an implicitly simulated solvent and SMD continuum solvation model.[10]

Anion-anion stacked

E(RB97D3/def2TZVP//RB97D3/6-31G*) = -1370.014201 Hartree

8	4.685590000	-1.764100000	-3.570636000
8	5.469100000	-0.095602000	-1.653734000
8	5.125537000	-1.660893000	-0.034819000
8	4.355867000	-1.967042000	-5.768008000
6	4.656407000	-2.248814000	-2.274753000
6	4.276378000	-2.512543000	-4.669013000
6	3.791358000	-3.864870000	-4.405532000
6	3.315693000	-4.655640000	-5.472145000
1	3.318069000	-4.242953000	-6.479909000
6	2.835141000	-5.938134000	-5.225488000
1	2.454439000	-6.545724000	-6.046051000
6	2.824110000	-6.445098000	-3.908082000
1	2.436915000	-7.447037000	-3.719435000
6	3.290361000	-5.674694000	-2.846217000
1	3.267974000	-6.060691000	-1.826824000
6	3.779406000	-4.367564000	-3.073862000
6	4.235745000	-3.513586000	-2.013085000

1	4.206427000	-3.851776000	-0.981227000
6	5.125597000	-1.236806000	-1.229684000
8	1.360417000	-1.721979000	-3.012963000
8	1.949142000	-0.734068000	-0.607484000
8	1.696017000	-2.779519000	0.364103000
8	1.265821000	-1.251330000	-5.190856000
6	1.159220000	-2.552628000	-1.926755000
6	0.995377000	-2.065619000	-4.310325000
6	0.328457000	-3.352276000	-4.491116000
6	-0.070723000	-3.755295000	-5.781775000
1	0.114000000	-3.091224000	-6.625138000
6	-0.684207000	-4.991729000	-5.965148000
1	-0.991584000	-5.306323000	-6.962650000
6	-0.902017000	-5.840957000	-4.858869000
1	-1.378203000	-6.810928000	-5.008384000
6	-0.509629000	-5.455352000	-3.579674000
1	-0.670791000	-6.115388000	-2.726728000
6	0.112957000	-4.202188000	-3.370080000
6	0.557790000	-3.761219000	-2.077479000
1	0.426770000	-4.393990000	-1.203565000
6	1.651095000	-1.963220000	-0.604872000

Molecule-molecule stacked

E (RB97D3/def2TZVP//RB97D3/6-31G*) = -1370.943321 Hartree

1	5.831802000	-0.082792000	-0.237634000
8	4.816539000	-1.769062000	-3.209305000
8	5.587879000	-0.497600000	-1.093850000
8	4.949901000	-2.165804000	0.321469000
8	4.602650000	-1.602351000	-5.422507000
6	4.652555000	-2.454529000	-2.028604000
6	4.437596000	-2.312791000	-4.440581000
6	3.886127000	-3.668864000	-4.422189000
6	3.490927000	-4.271302000	-5.630884000
1	3.612778000	-3.724319000	-6.564032000
6	2.930635000	-5.548066000	-5.617312000
1	2.615939000	-6.012220000	-6.551293000
6	2.755782000	-6.234201000	-4.398933000
1	2.303966000	-7.225771000	-4.396979000
6	3.143052000	-5.648851000	-3.195150000
1	2.999579000	-6.171211000	-2.249539000
6	3.717450000	-4.359381000	-3.188105000
6	4.122821000	-3.704359000	-1.976613000
1	3.998459000	-4.190521000	-1.012505000
6	5.072236000	-1.714226000	-0.813798000
8	1.380892000	-1.711811000	-3.292823000
8	2.226579000	-0.451863000	-1.203041000
8	1.616305000	-2.116070000	0.229689000
8	1.244833000	-1.599745000	-5.515890000

6	1.156200000	-2.356359000	-2.100091000
6	0.977324000	-2.255303000	-4.517910000
6	0.288181000	-3.544369000	-4.471267000
6	-0.128551000	-4.148352000	-5.672212000
1	0.057205000	-3.638200000	-6.615927000
6	-0.761210000	-5.390277000	-5.640909000
1	-1.081340000	-5.860378000	-6.570570000
6	-0.979886000	-6.043634000	-4.410877000
1	-1.470023000	-7.017328000	-4.395583000
6	-0.571302000	-5.457233000	-3.214681000
1	-0.732991000	-5.961688000	-2.262059000
6	0.068362000	-4.197871000	-3.225985000
6	0.526784000	-3.557497000	-2.025700000
1	0.386527000	-4.026433000	-1.054977000
6	1.676944000	-1.650239000	-0.903961000
1	2.554508000	-0.061767000	-0.363296000

Anion-molecule stacked

E (RB97D3/def2TZVP//RB97D3/6-31G*) = -1370.480963 Hartree

1	5.850388000	-0.076847000	-0.288417000
8	4.835234000	-1.784877000	-3.248620000
8	5.609102000	-0.496780000	-1.142560000
8	4.974822000	-2.155475000	0.285006000
8	4.649387000	-1.644666000	-5.465836000
6	4.654362000	-2.453548000	-2.060403000
6	4.466417000	-2.340896000	-4.475730000
6	3.907303000	-3.693191000	-4.447244000
6	3.523356000	-4.308827000	-5.653614000
1	3.658019000	-3.772810000	-6.591462000
6	2.958560000	-5.582885000	-5.632055000
1	2.652539000	-6.057293000	-6.563897000
6	2.767559000	-6.253422000	-4.406882000
1	2.311582000	-7.243206000	-4.397853000
6	3.143248000	-5.655159000	-3.206169000
1	2.985802000	-6.165412000	-2.256124000
6	3.722236000	-4.367311000	-3.206714000
6	4.118808000	-3.699953000	-1.998897000
1	3.978782000	-4.171991000	-1.030295000
6	5.079004000	-1.705066000	-0.852466000
8	1.431847000	-1.723196000	-3.303182000
8	2.335680000	-0.482292000	-1.137967000
8	1.644583000	-2.171688000	0.223481000

8	1.299578000	-1.606486000	-5.526844000
6	1.202018000	-2.347235000	-2.091875000
6	1.021876000	-2.257052000	-4.521726000
6	0.313460000	-3.533208000	-4.479425000
6	-0.103389000	-4.138506000	-5.682033000
1	0.096472000	-3.633448000	-6.626064000
6	-0.750797000	-5.371169000	-5.652300000
1	-1.070386000	-5.842666000	-6.581736000
6	-0.985993000	-6.013957000	-4.418099000
1	-1.488584000	-6.981814000	-4.400577000
6	-0.579145000	-5.426376000	-3.222691000
1	-0.755051000	-5.926078000	-2.269522000
6	0.078468000	-4.173918000	-3.230472000
6	0.542481000	-3.533209000	-2.031716000
1	0.390391000	-3.998311000	-1.061079000
6	1.776118000	-1.591798000	-0.895062000

S6: References

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