Electronic Supplementary Material (ESI) for CrystEngComm.

SUPPLEMENTARY MATERIAL

Mechanochemical Synthesis of Phthalimides with Crystal Structures of Intermediates and Products.

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List of supplementary material

Figure S1. Powder X-ray diffractograms of solids obtained during synthesis of N-phthaloyl-2,6-dimethylaniline (**3ai**)
a) starting product (phthalic anhydride) and ground solid of **1a** and **2i**.
b) solid obtained after grinding of **1a** and **2i** and heating to 200°C.
c) pattern simulated from the single crystal X-ray structure.

Figure S2. X-ray diffraction analysis of the solid corresponding to 4-carboxylic-N-phthaloyl-2,6-dimethylaniline (**3bi**), obtained after grinding of **1b** and **2i** and heating to 200°C. a) Powder diffractograms recorded before and after heating of the ground sample and b) single crystal structure obtained by recrystallization from Toluene/MeOH or c) from a solution in EtOAc. d, e) patterns simulated (Mercury Program) from the single crystal X-ray structures.

Figure S3. Crystal structure of 4-carboxylic-N-phthaloyl-p-anisole (**3bn**, m.p. >260°C)

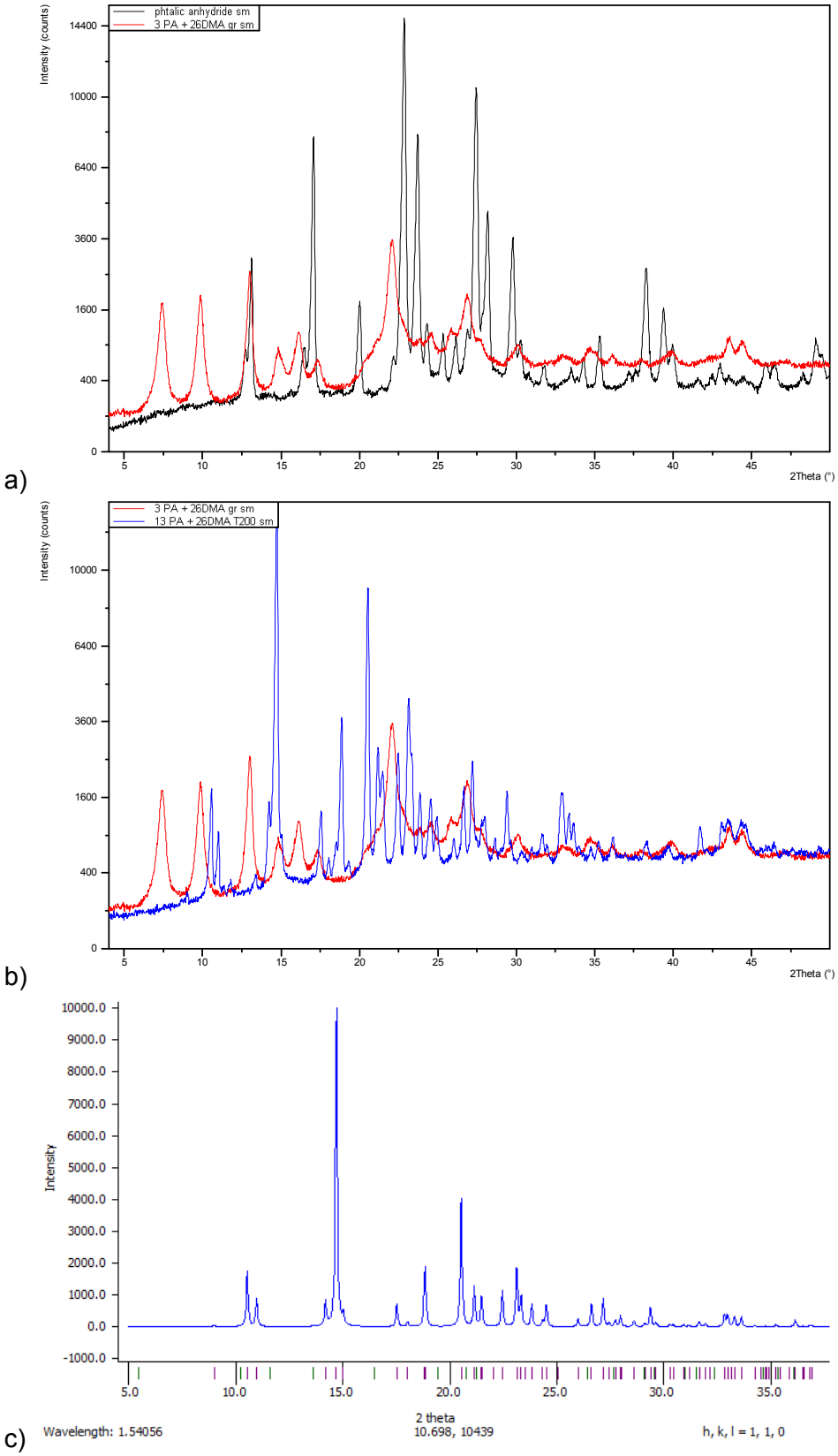
Figure S4. Solid-state reaction of 3-nitrophtalic anhydrates (**1c**) with 2,6-dibromoaniline (**2k**) leads to an open product of 3-nitro-N-phthaloyl-2,6-dibromoaniline (**3ck**).

Figure S5. Structure of the intermediate co-crystal observed during the reaction of 4-nitrophthalic anhydrate (**1d**) and 4-methylaniline (**2m**). Two perpendicular views (a, b) of the $\pi-\pi$ stacking 1:1 co-crystal. c) H-bonding network (dashed line).

Nuclear Magnetic Resonance (NMR).

Crystallographic data

Table S1. Selected H-bonding interactions



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b) solid obtained after grinding of **1a** and **2i** and heating to 200°C.
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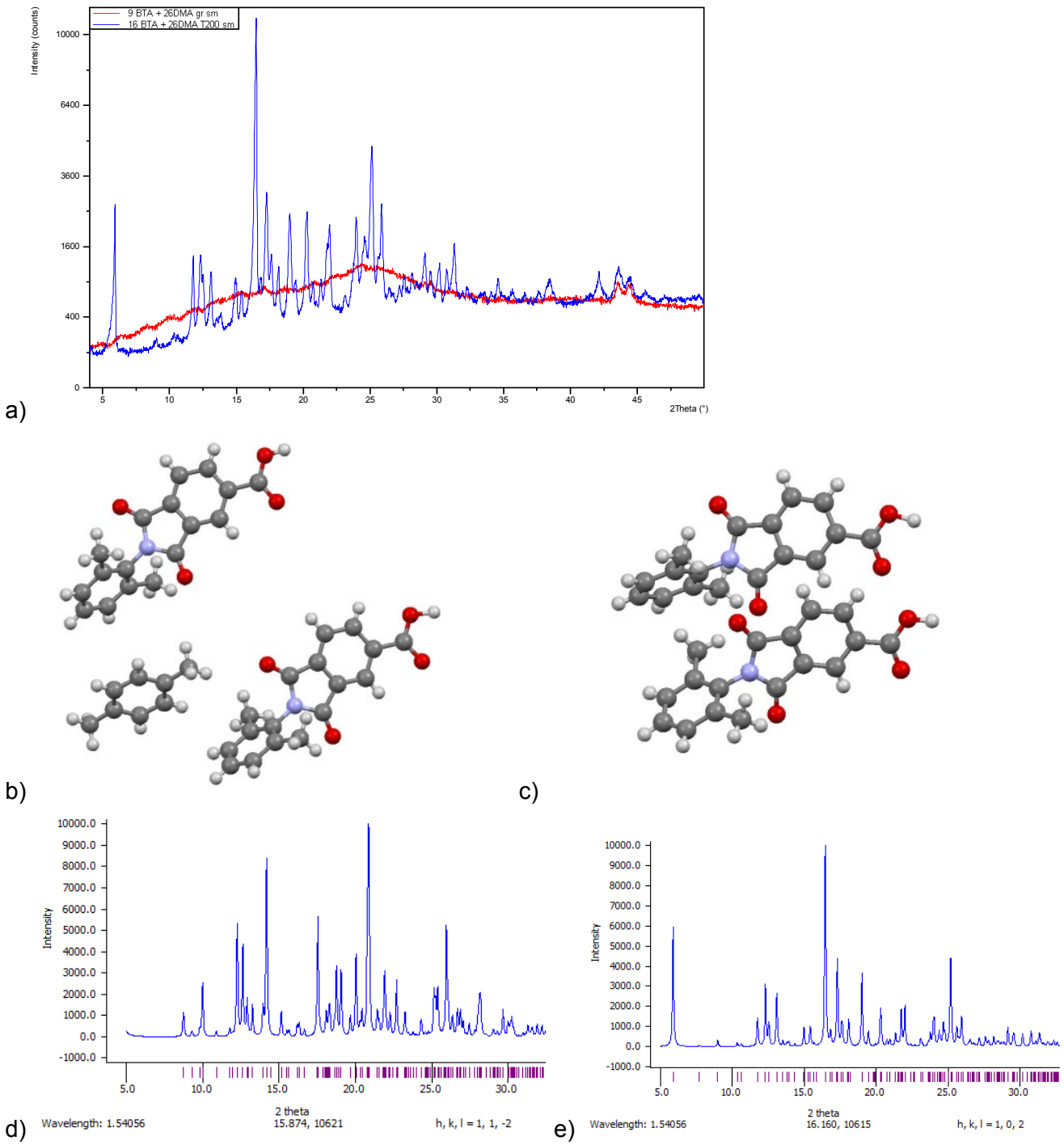

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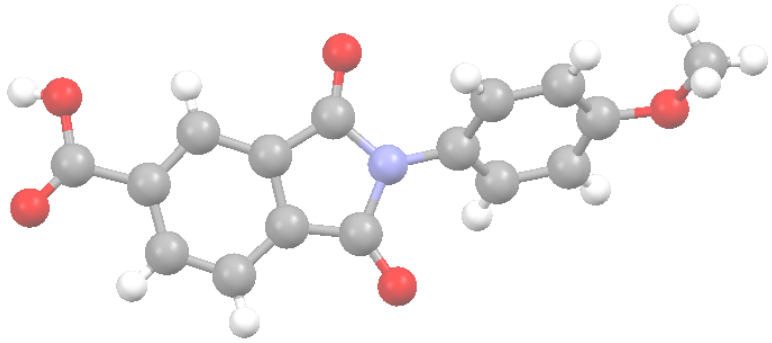

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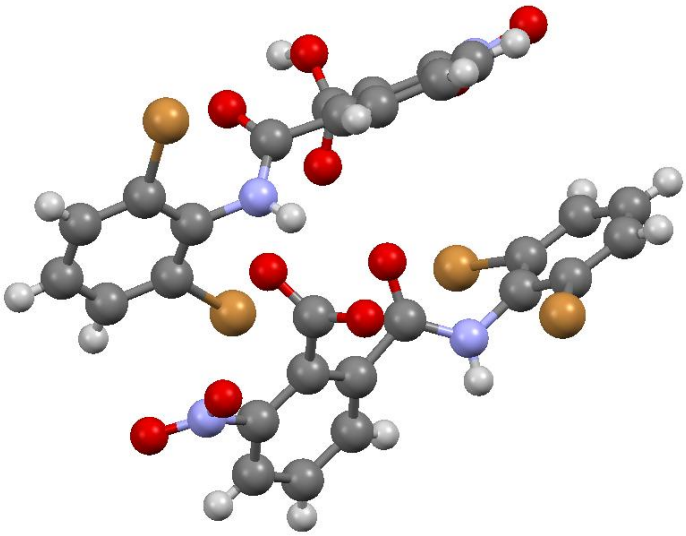
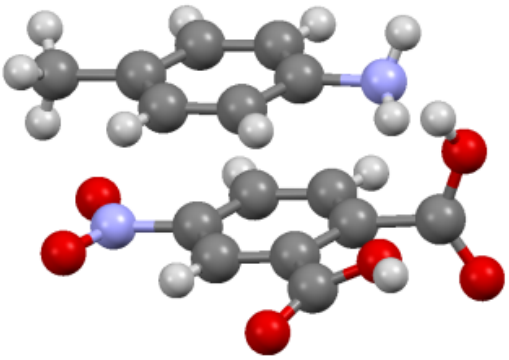


Figure S4. Solid-state reaction of 3-nitrophthalic anhydrates (**1c**) with 2,6-dibromoaniline (**2k**) leads to an open product of 3-nitro-N-phthaloyl-2,6-dibromoaniline (**3ck**).

a)



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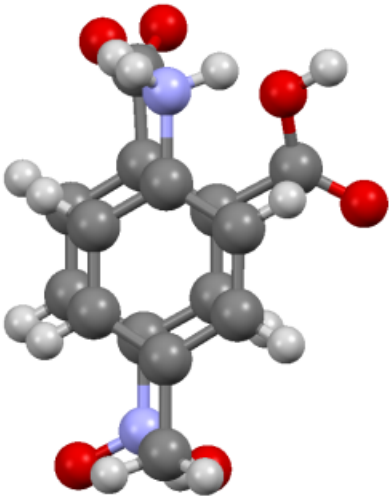

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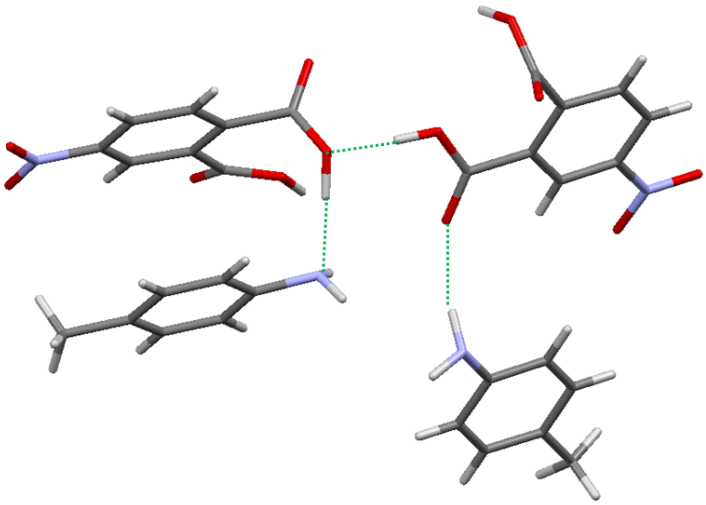

Figure S5. Structure of the intermediate co-crystal observed during the reaction of 4-nitrophthalic anhydrite (**1d**) and 4-methylaniline (**2m**). Two perpendicular views (a, b) of the π–π stacking 1:1 co-crystal. c) H-bonding network (dashed line).

Nuclear Magnetic Resonance (NMR).

All NMR (^{1}H) were recorded on Jeol spectrometer (JNM EX-400) at 25°C. Chemical shifts are reported in parts per million (ppm) using the solvent residual peak as reference ($CDCl_3$: 7.26 ppm; DMSO-d_6: 2.50 ppm; CD_3OD: 3.31 ppm). Coupling constants (J) are reported in Hertz (Hz). The resonance multiplicity is described as s for singlet, bs for broad singlet, d for doublet, t for triplet, q for quadruplet and m for multiplet.

N-phthaloyl-2,6-dimethylaniline (3ai) : $_1$H NMR (400MHz, $CDCl_3$) : δ (ppm) = 2.16 (s, 6H), 7.19 (d, 2H, J=7.6Hz), 7.27 (t, 1H, J=7.5Hz), 7.80 (m, 2H), 7.96 (m, 2H)

N-phthaloyl-2,6-dibromoaniline (3ak) : $_1$H NMR (400MHz, DMSO-*d6*) : δ (ppm) = 6.43 (t, 1H, J=8.0Hz), 7,38 (d, 2H, J=8.0Hz), 7.97 (m, 2H), 8.06 (m, 2H)

N-phthaloyl-p-anisole (3an) : $_1$H NMR (400MHz, DMSO-*d6*) : δ (ppm) = 3.78 (s, 3H), 7.03 (dt, 2H, J1=8.9, J2=2.8), 7.32 (dt, 2H, J_1=8.9, J_2=2.8), 7.86 (m, 2H), 7.91 (m, 2H)

4-carboxylic-N-phthaloyl-2,6-dimethylaniline (3bi) : $_1$H NMR (400MHz, $CDCl_3$) : δ (ppm) = 2.16 (s, 6H), 7.20 (d, 2H, J=7.6Hz), 7.29 (t, 1H, J=7.6Hz), 8.09 (d, 1H, J=7.8), 8.56 (dd, 1H, J_1=7.8Hz, J_2=1,4), 8.68 (s, 1H)

4-carboxylic-N-phthaloyl-2,6-dichloroaniline (3bj) : $_1$H NMR (400MHz, DMSO-*d6*) : δ (ppm) = 7.63 (t, 1H, J=8.1Hz), 7.75 (d, 2H, J=8.2Hz), 8.09 (td, 1H, J_1=8.0Hz, J_2=1,8Hz), 8.19 (d, 1H, J=7,8Hz), 8.23 (d, 1H, J=1,6Hz)

4-carboxylic-N-phthaloyl-2,6-dibromoaniline (3bk) : $_1$H NMR (400MHz, DMSO-*d6*) : δ (ppm) = 7.45 (t, 1H, J=8.1Hz), 7.89 (d, 2H, J=8,0Hz), 8.20 (d, 1H, J=7.8Hz), 8.40 (s, 1H), 8.48 (dd, 1H, J_1=7.8Hz, J_2=1.4Hz)

4-carboxylic-N-phthaloyl-2,4-dichloroaniline (3bl) : $_1$H NMR (400MHz, DMSO-*d6*) : δ (ppm) = 7.47 (d, 1H, J=8.5) (7.66 (d, 1H, J=1.8Hz), 7.69 (dd, 1H, J_1=8.3Hz, J_2=2.2Hz), 8.02-8.13 (m, 3H)

4-carboxylic-N-phthaloyl-4-méthylaniline (3bm) : $_1$H NMR (400MHz, $CDCl_3$) : δ (ppm) = 2.42 (s, 3H), 7.32 (s, 4H), 8.07 (d, 1H, J=7,8Hz), 8.54 (dd, 1H, J_1=7.8Hz, J_2=1.4Hz), 8.66 (sm, 1H)

4-carboxylic-N-phthaloyl-p-anisole (3bn) : $_1$H NMR (400MHz, DMSO-*d6*) : δ (ppm) = 3.78 (s, 3H), 7.05 (d, 2H, J=8.9Hz), 7.33 (d, 2H, J=8.9Hz), 8.04 (d, 1H, J=7.8Hz), 8.26 (s, 1H), 8.38 (d, 1H, J=7.6Hz)

4-carboxylic-N-phthaloyl-3-nitroaniline (3bo) : $_1$H NMR (400MHz, DMSO-*d6*) : δ (ppm) = 7.84 (t, 1H, J=8.13Hz), 7.95 (d, 1H, J=8.13Hz), 8.10 (d, 1H, J=7.8Hz) 8.30 (dd, 1H, J_1=7.1Hz, J_2=2.3Hz), 8.31 (s, 1H), 8.39 (t, 1H, J=2.3Hz), 8.41 (dd, 1H, J_1=7.8Hz, J_2=1.1Hz)

4-carboxylic-N-phthaloyl-2-carboxylicaniline (3bp) : $_1$H NMR (400MHz, DMSO-*d6*) : δ (ppm) = 6.46 (t, 1H, J=7.4Hz), 6.69 (d, 1H, J=8.5Hz), 7.18 (td, 1H, J_1=7.7Hz, J_2=1.5Hz), 7.64 (dd, 1H, J_1=8.1Hz, J_2=1.7Hz), 8.16 (d, 1H, J=8.0Hz), 8.35 (s, 1H), 8.93 (dd, 1H, J=7.9Hz)

3-nitro-N-phthaloyl-2,6-dimethylaniline (3ci) : $_1$H NMR (400MHz, DMSO-*d6*) : δ (ppm) = 2.26 (s, 6H), 7.02 (s, 2H), 7.09 (s, 1H), 7.76 (t, 1H, J=8.1Hz), 8.13 (d, 1H, J=7.8Hz), 8.20 (d, 1H, J=8.0Hz)

3-nitro-N-phthaloyl-2,6-dichloroaniline (3cj) : $_1$H NMR (400MHz, DMSO-*d6*) : δ (ppm) = 6.54 (t, 1H, J=7.9Hz), 7.19 (d, 2H, J=8.0Hz), 8.17 (t, 1H, J=8.2Hz), 8.36 (d, 1H, J=7.6Hz), 8.47 (d, 1H, J=8.0Hz)

3-nitro-N-phthaloyl-2,6-dibromoaniline (3ck) : $_1$H NMR (400MHz, DMSO-*d6*) : δ (ppm) = 7.13 (t, 1H, J=8.0Hz), 7.68 (d, 2H, J=8.0Hz), 7.77 (t, 1H, J=8.0Hz), 8.12 (d, 1H, J=7.8Hz), 8.20 (d, 1H, J=8.2Hz)

3-nitro-N-phthaloyl-4-methylaniline (3cm) : $_1$H NMR (400MHz, DMSO-*d6*) : δ (ppm) = 2.34 (3H), 7.29 (dd, 4H, J1=8.5Hz, J2= 2.8Hz), 8.07 (t, 1H, J=7.8Hz), 8.21 (d, 1H, J=7.8Hz), 8.30 (d, 1H, J=7.8Hz)

3-nitro-N-phthaloyl-p-anisole (3cn) : $_1$H NMR (400MHz, DMSO-*d6*) : δ (ppm) = 3.78 (s, 3H), 7.31 (dd, 2H, J_1=8.9Hz, J_2=2.2Hz), 7.38 (dd, 2H, J_1=8.9Hz, J_2=2.2Hz), 8.07 (t, 1H, J=7.8Hz), 8.19 (dd, 2H, J_1=7.8Hz, J_2 =1.14Hz)

3-nitro-N-phthaloyl-3-nitroaniline (3co) : $_1$H NMR (400MHz, DMSO-*d6*) : δ (ppm) = 7.62 (t, 1H, J=8.2Hz), 7.84 (t, 2H, J=8.0Hz), 7.95 (dd, 1H, J_1=7.9Hz, J_2=1.9Hz), 8.29 (dd, 1H, J_1=7.9Hz, J_2=1.0Hz), 8.37 (dd, 1H, J_1=8.2Hz, J_2=1.1Hz), 8.60 (t, 1H, J=2.1Hz)

4-nitro-N-phthaloyl-2,6-dimethylaniline (3di) : $_1$H NMR (400MHz, DMSO-*d6*) : δ (ppm) =7.22 (d, 2H, J=7.6Hz), 7.31 (t, 1H, J=7.7Hz), 8.24 (d, 1h, J=8.0Hz), 8.46 (d, 1H, J=1.8Hz), 8.69 (dd, 1H, J_1=8.1Hz, J_2=1.9Hz)

4-nitro-N-phthaloyl-2,6-dibromoaniline (3dk) : $_1$H NMR (400MHz, DMSO-*d6*) : δ (ppm) = 7,47 (t, 1H, J=8.1Hz), 7.91 (d, 2H, J=8.0Hz), 8.35 (d, 1H, J=8.2Hz), 8.49 (d, 1H, J=2.1Hz), 8.75 (dd, 1h, J_1=8.1Hz, J_2=1.9Hz)

4-nitro-N-phthaloyl-4-methylaniline (3dm) : $_1$H NMR (400MHz, DMSO-*d6*) : δ (ppm) = 2.34 (s, 3H), 7.31 (s, 4H), 8.17 (d, 1H, 8.2Hz), 8.54 (m, 1H), 8.64 (m, 1H)

4-nitro-N-phthaloyl-*p*-anisole (3dn) : $_1$H NMR (400MHz, DMSO-*d6*) : δ (ppm) = 3.79 (s, 3H), 7.06 (d, 2H, J=8.7Hz), 7.35 (d, 2H, J=8.9Hz), 8.17 (d, 1H, J=8.2Hz), 8.54 (d, 1H, J=1.8Hz), 8.55 (dd, 1H, J_1=8.1Hz, J_2=1.9Hz)

4-nitro-N-phthaloyl-3-nitroaniline (3do) : $_1$H NMR (400MHz, DMSO-*d6*) : δ (ppm) = 7.86 (t, 1H, J=8.1Hz), 7.85 (t, 1H, J=8.0Hz), 8.24 (d, 1H, J=8.2Hz), 8.31 (m, 1H), 8.40 (t, 1h, J=2.1Hz), 8.60 (d, 1H, J=2.1Hz), 8.68 (dd, 1H, J_1=8.1 Hz, J_2=1.9Hz)

Crystallographic data.

Single crystal X-ray diffraction was performed on a Gemini Ultra R system (4-circle kappa platform, Ruby CCD detector) using Mo (λ = 0.71073 Å) or Cu Kα radiation (λ = 1.54056 Å). Selected crystals were mounted on the tip of a quartz pin using cyanoacrylate (Commercial glue). Cell parameters were estimated from a pre-experiment run and full data sets collected at room temperature. Structures were solved by direct methods with sir92 (v.3.0) program and then refined on F^2 using SHELXL-97 software. Non-hydrogen atoms were anisotropically refined and the hydrogen atoms (not implicated in H-bonds) in the riding mode with isotropic temperature factors fixed at 1.2 times U(eq) of the parent atoms (1.5 times for methyl groups). Hydrogen atoms implicated in H-bonds were localized by Fourier difference maps (ΔF).

Crystal Data for PA-DMA (3ai) *CCDC 1021624***.** Prism colourless crystals, orthorhombic, Pbc21, a = 9.837(2), b = 16.124(4), c = 8.643(3)Å, α =90.00, β = 90.00, γ = 90.00 °, V = 1370.9(6) Å^3, Z = 4, ρ_{calc} = 1.217g cm^{-3}, F_{000} = 528, λ Mo Kα = 0.71073 Å, θ_{max} = 25.0°, 4759 total measured reflections, 1994 independent reflections (R_{int} = 0.031), 1322 observed reflections (I > 2 σ(I)), μ = 0.081 mm^{-1}, 136 parameters, R_1 (observed data) = 0.0880, S = GooF = 1.09, Δ/s.u. = 0.00, residual ρ_{max} = 0.27 e Å^{-3}, ρ_{min} = -0.26 e Å^{-3}.

Crystal Data for BTA-DMA 1st form (3bi) *CCDC 1021625***.** Plate colourless crystals, triclinic, P-1, a = 8.3591(3), b = 10.4196(7), c = 19.0455(9)Å, α =88.407(5), β = 88.481(3), γ = 76.340(4)°, V = 1610.95(15) Å^3, Z = 1, ρ_{calc} = 1.311g cm^{-3}, F_{000} = 665, λ Mo Kα = 0.71073 Å, θ_{max} = 25.0°, 11980 total measured reflections, 5663 independent reflections (R_{int} = 0.024), 3983 observed reflections (I > 2 σ(I)), μ = 0.093 mm^{-1}, 438 parameters, R_1 (observed data) = 0.0468, S = GooF = 0.99, Δ/s.u. = 0.02, residual ρ_{max} = 0.16 e Å^{-3}, ρ_{min} = -0.17 e Å^{-3}.

Crystal Data for BTA-DMA 2nd form (3bi) *CCDC 1021626***.** Plate colourless crystals, triclinic, P-1, a = 8.4040(5), b = 8.4040(5), c = 15.240(1)Å, α =97.881(6), β = 93.354(5), γ = 96.810(6)°, V = 1468.73(18) Å^3, Z = 4, ρ_{calc} = 1.335 g cm^{-3}, F_{000} = 616, λ Mo Kα = 0.71073 Å, θ_{max} = 23.3°, 10179 total measured reflections, 4188 independent reflections (R_{int} = 0.078), 2204 observed reflections (I > 2 σ(I)), μ = 0.096 mm^{-1}, 400 parameters, R_1 (observed data) = 0.0705, S = GooF = 1.01, Δ/s.u. = 0.03, residual ρ_{max} = 0.19 e Å^{-3}, ρ_{min} = -0.21 e Å^{-3}.

Crystal Data for 3NPA-DBA open form (3ck) *CCDC 1021627***.** Needle colourless crystals, triclinic, P_{-1}, a = 9.188(5), b = 13.284(7), c = 14.477(8)Å, α = 68.21(5), β = 81.24(4), γ = 75.69(4) °, V = 1586.2(16) Å^3, Z = 2, ρ_{calc} = 1.857 g cm^{-3}, F_{000} = 862, λ Mo Kα = 0.71073 Å, θ_{max} = 25.0 °, 11937 total measured reflections, 5562 independent reflections (R_{int} = 0.052), 3222 observed reflections (I > 2 σ(I)), μ = 5.136 mm^{-1}, 415 parameters, R_1 (observed data) = 0.0655, S = GooF = 1.04, Δ/s.u. = 0.00, residual ρ_{max} = 0.88 e Å^{-3}, ρ_{min} = -0.59 e Å^{-3}.

Crystal Data for 3NPA-pAni (3cn) *CCDC 1021628***.** Needle yellow crystals, Monoclinic, $P2_1$, a = 3.8289(1), b = 23.3314(7), c = 7.4554(2)Å, α = 90, β = 98.153(3), γ = 90°, V = 659.3(1) Å^3, Z = 2, ρ_{calc} = 1.502 g cm^{-3}, F_{000} = 308, λ Cu Kα = 1.54184 Å, θ_{max} = 66.6°, 5907 total measured reflections, 2304 independent reflections (R_{int} = 0.0182), 2285 observed reflections (I > 2 σ(I)), μ = 0.977 mm^{-1}, 200 parameters, R_1 (observed data) = 0.0270, S = GooF = 1.08, Δ/s.u. = 0.001, residual ρ_{max} = 0.16 e Å^{-3}, ρ_{min} = -0.14 e Å^{-3}.

Crystal Data for 4NPA-DBA (3dk) *CCDC 1021629***.** Plate colourless crystals, monoclinic, *I2/a*, a = 14.8231(9), b = 7.7177(6), c = 25.714(2)Å, α = 90, β = 97.692(7), γ = 90 °, V = 2915.2(4) Å^3, Z = 8, ρ_{calc} = 1.941g cm^{-3}, F_{000} = 1648, λ Mo Kα = 0.71073 Å, θ_{max} = 25.0°, 6774 total measured reflections, 2563 independent reflections (R_{int} = 0.079), 1465 observed reflections (I > 2 σ(I)), μ = 5.580 mm^{-1}, 392 parameters, R_1 (observed data) = 0.0491, S = GooF = 0.96, Δ/s.u. = 0.00, residual ρ_{max} = 0.36 e Å^{-3}, ρ_{min} = -0.40 e Å^{-3}.

Crystal Data for 4NPA-DBA open form (3dk) Crystal Data for 4NPA-DBA open form (**3dk**). Plates colourless crystals, monoclinic, *P2$_1$/n*, a = 14.0897(3), b = 4.8183(1), c = 22.6757(3)Å, α = 90, β = 90.555(9), γ = 90 °, V = 1539.3(1) Å^3, Z = 4, ρ_{calc} = 1.916g cm^{-3}, F_{000} = 864, λ Cu Kα = 1.54184 Å, θ_{max} = 66.6°, 8457 total measured reflections, 2710 independent reflections (R_{int} = 0.0344), 2466 observed reflections (I > 2 σ(I)), μ = 6.946 mm^{-1}, 216 parameters, R_1 (observed data) = 0.0465, S = GooF = 1.07, Δ/s.u. = 0.00, residual ρ_{max} = 0.53e Å^{-3}, ρ_{min} = -0.68 e Å^{-3}.

Crystal Data for 4NPA-pAni (3dn) *CCDC 1021631***.** Triangular yellow crystals, monoclinic, *Pn*, a = 6.9750(12), b = 3.876(1), c = 23.998(3)Å, α = 90, β = 91.227(12), γ = 90 °, V = 648.6(2) Å^3, Z = 2, ρ_{calc} = 1.527g cm^{-3}, F_{000} = 308, λ Mo Kα = 0.71073 Å, θ_{max} = 23.3°, 1900 total measured reflections, 1462 independent reflections (R_{int} = 0.045), 1224 observed reflections (I > 2 σ(I)), μ = 0.117 mm^{-1}, 200 parameters, R_1 (observed data) = 0.0724, S = GooF = 1.14, Δ/s.u. = 0.00, residual ρ_{max} = 0.32 e Å^{-3}, ρ_{min} = -0.34 e Å^{-3}.

Crystal Data for 4NPA-pTol co-crystal (3dm) *CCDC 1021632***.** Triangular yellow crystals, Orthorhombic, Fdd2 , a = 59.519(2), b = 12.942(5), c = 7.623(2)Å, α = 90, β = 90, γ = 90 °, V = 5872(3) Å^3, Z = 16, ρ_{calc} = 1.440g cm^{-3}, F_{000} = 2656, λ Mo Kα = 0.71073 Å, θ_{max} = 25.0°, 20263 total measured reflections, 2560 independent reflections (R_{int} = 0.052), 2335 observed reflections (I > 2 σ(I)), μ = 0.113 mm^{-1}, 217 parameters, R_1 (observed data) = 0.0433, S = GooF = 1.01, Δ/s.u. = 0.04, residual ρ_{max} = 0.26 e Å^{-3}, ρ_{min} = -0.15 e Å^{-3}.

Table S1. Selected H-bonding interactions (

Crystal Data for 3NPA-DBA (3ck).

D-H…A	d D-H (Å)	d H…A(Å)	d D_H…A(Å)	Angle D_H…A (°)	
BTA-DMA 1st form (3ck).					
O4 -- H4O .. O23	0.8200	1.8400	2.652(2)	169.00	-x,2-y,1-z
O24 -- H24O .. O3	0.8200	1.8500	2.652(2)	168.00	-x,2-y,1-z
BTA-DMA 2nd form (3ck).					
O3 -- H3O .. O24	0.8200	1.8200	2.628(5)	170.00	-x,-y,1-z
O23 -- H23O .. O4	0.8200	1.8200	2.638(5)	172.00	-x,-y,1-z
3NPA-DBA (3ck).					
N1 -- H1 .. O21	0.8600	1.9800	2.829(7)	168.00	1+x,y,z
N21 -- H21 .. O1	0.8600	2.1100	2.924(7)	159.00	.
4NPA-DBA (3dk) open form.					
N1 -- H1 .. O1	0.867(13)	2.037(19)	2.878(3)	163(4)	x,-1+y,z
C12 -- H12 .. O4	0.9300	2.5900	3.183(7)	122	-1/2+x,1/2-y,1/2+z
4NPA-pTol (3dm).					
N20 -- H2N .. O4	0.9000	2.5900	3.019(3)	110.00	.
N20 -- H2N .. O2	0.9000	1.9400	2.789(3)	158.00	1-x,1/2-y,1/2+z
N20 -- H3N .. O2	0.8900	2.4500	2.928(3)	114.00	x,1/2+y,1/2+z
N20 -- H3N .. O3	0.8900	2.0700	2.913(3)	157.00	x,1/2+y,-1/2+z
O4 -- H4O .. O1	0.91(4)	1.58(4)	2.485(3)	175(3)	1-x,1/2-y,1/2+z
O1 -- H999 .. N20	0.99(10)	1.85(9)	2.824(3)	166(7)	.