SUPPORTING INFORMATION

Functionalized Cyano-OPVs as Melt-Processable Two-Photon Absorbers

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Single Crystal X-ray Diffraction Procedure for Dye A3

The dye **A3** was crystallized by dissolving in benzene, filling 1 inch of a glass Pasteur pipette which had previously been sealed with a Bunsen burner, then adding a layer of methanol (1 inch) and allowing diffusion into the benzene layer over time. Single-crystal diffraction study was done on a Bruker AXS SMART APEX II CCD diffractometer using monochromatic Mo Kα radiation with the omega scan technique. The unit cell was determined using SMART[1] and SAINT+.[2] Data collection for compound **A3** was conducted at 100 K (-173.5 °C). The structure was solved by the direct method and refined by full matrix least squares against F^2 with all reflections using SHELXTL.[3] Refinement of extinction coefficients was found to be insignificant. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in standard calculated positions and all hydrogen atoms were refined with an isotropic displacement parameter 1.2 times that of the adjacent carbon.

[1] Bruker Advanced X-ray Solutions. SMART for WNT/2000 (Version 5.628); Bruker AXS Inc.: Madison, WI, **1997–2002.**
[2] Bruker Advanced X-ray Solutions. SAINT (Version 6.45); Bruker AXS Inc.: Madison, WI, **1997–2003.**
[3] Bruker Advanced X-ray Solutions. *SHELXTL* (Version 6.10); Bruker AXS Inc.: Madison, WI, **2000**.

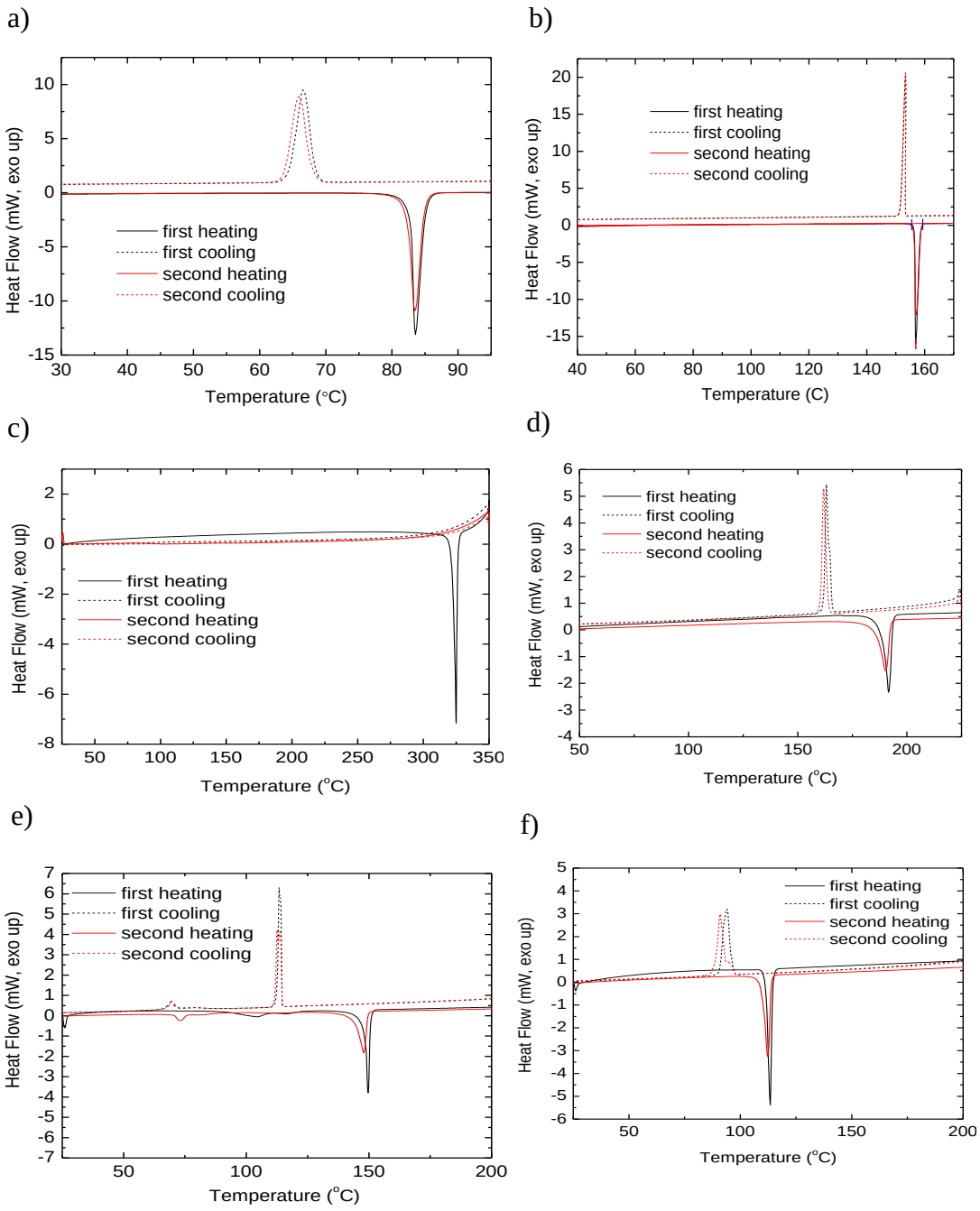

Figure S1. Differential scanning calorimetry (DSC) traces (heating rate 10 °C/min) of a) **A4**, b) **B2**, c) **C1**, d) **C2**, e) **D1**, and f) **D2**.

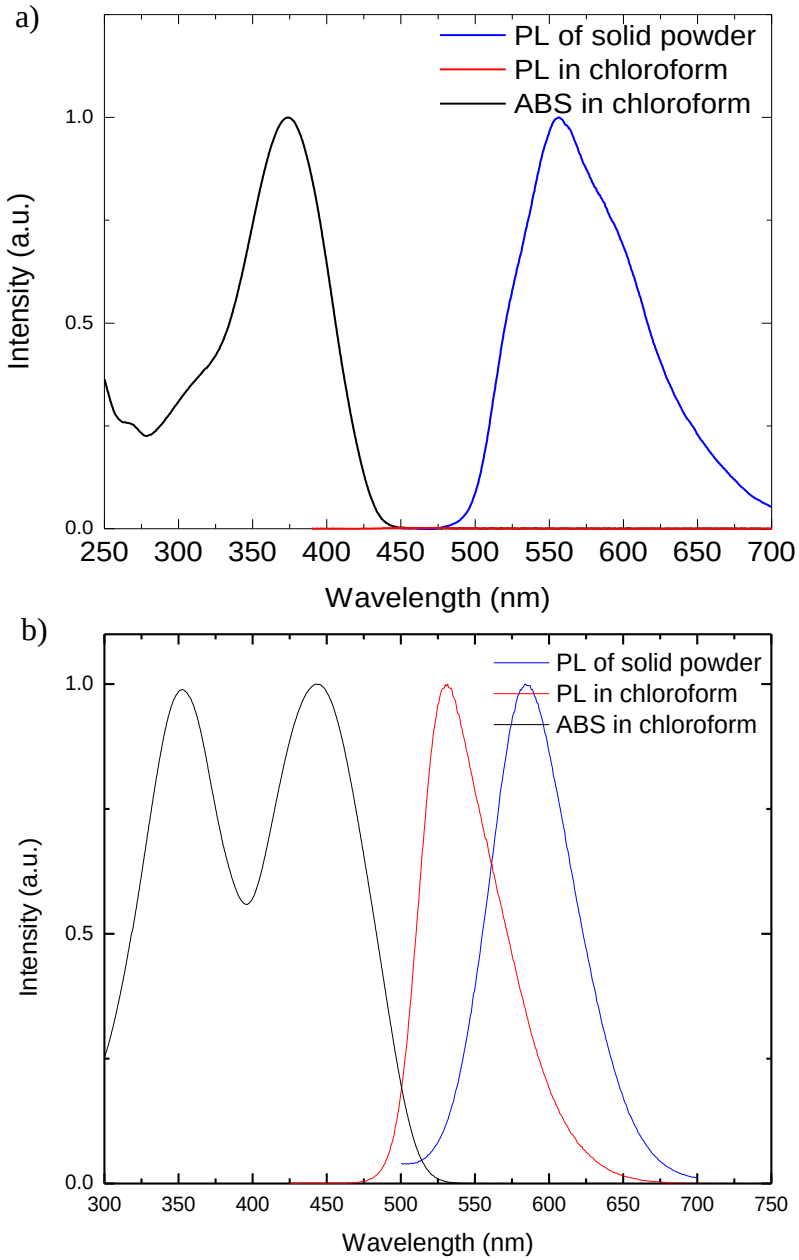

Figure S2. UV-Vis absorbance and fluorescence spectra (excitation at 365 nm) of a $CHCl_3$ solution and solid powder of a) **C1** and b) **D2**.

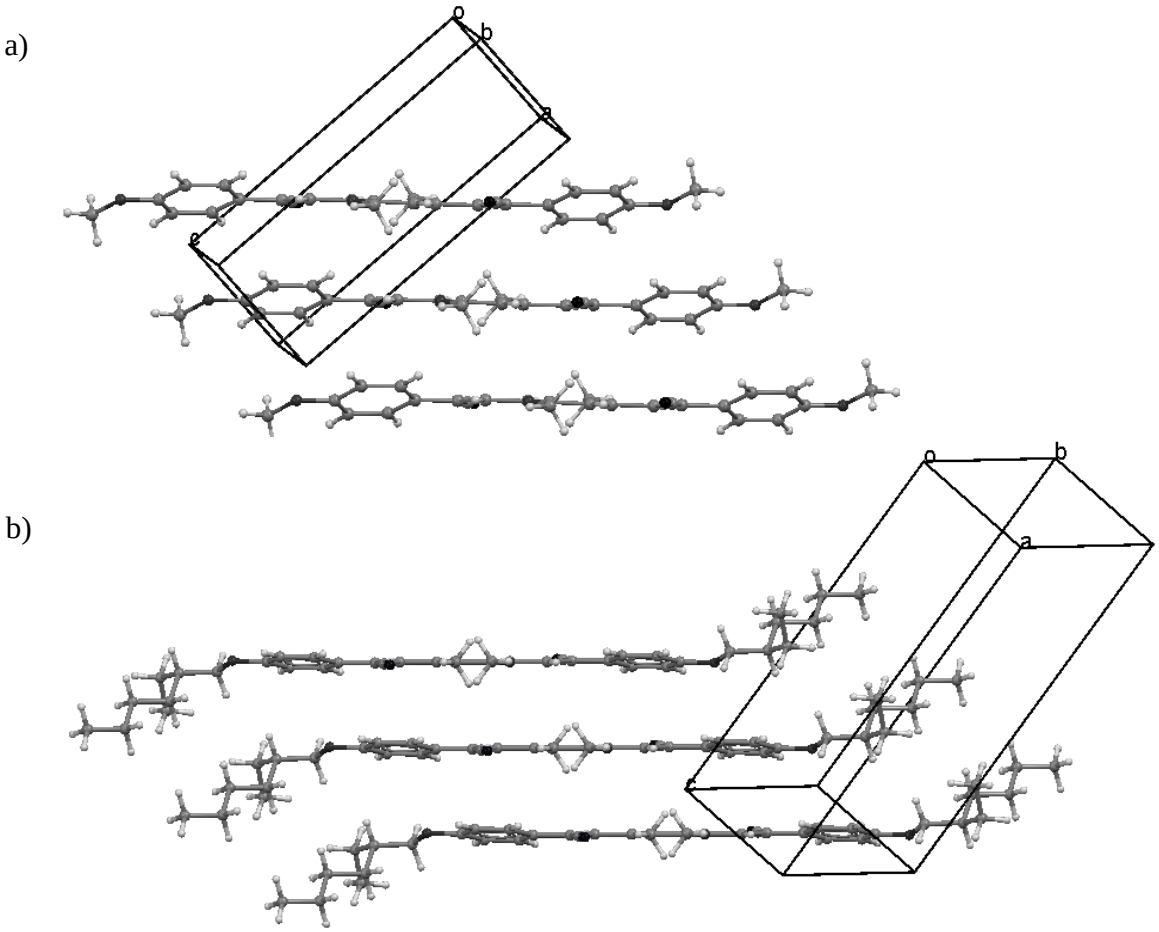

Figure S3. Crystal structures for a) **A1** and b) **A3**.

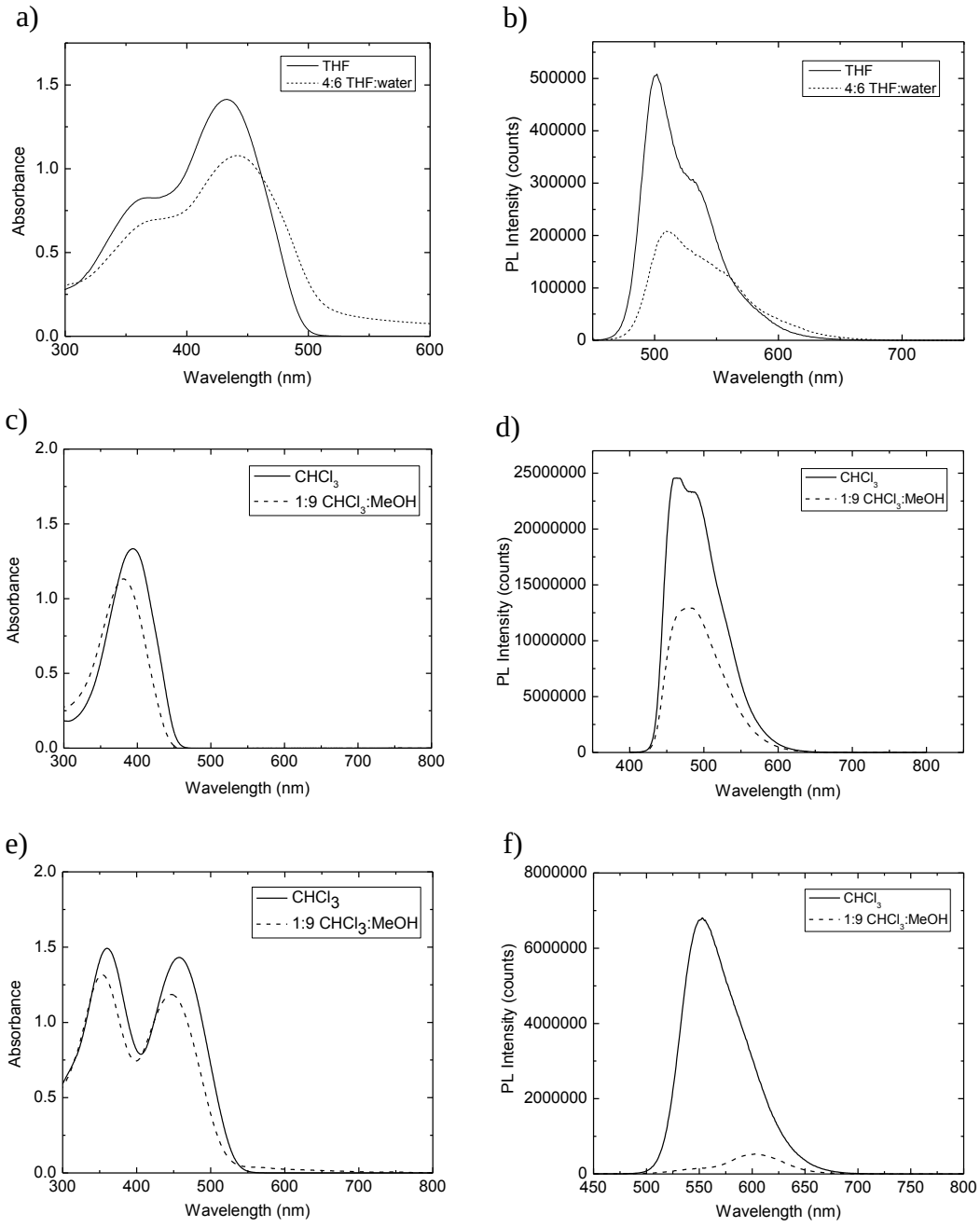

Figure S4. Excimer screening experiments for dyes **A3** (a,b), **B2** (c,d), and **C2** (e,f). The absorbance (a,c,e) and PL spectra (b,d,f) in a good solvent and a good solvent:poor solvent mixture (labeled in the figure) were measured for each dye at the same concentration (~4-5x10^{-5} M).

Table S1. Crystal data and structure refinement for **A3**.

Identification code	brianmakowski1_0m
Empirical formula	C42 H52 N2 O4
Formula weight	648.86
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a=5.7621(11) A alpha=93.949(2) deg. b=9.2731(17) A beta=93.856(2) deg. c=16.516(3) A gamma=92.524(2) deg.
Volume	877.4(3) A^3
Z, Calculated density	1, 1.228 Mg/m^3
Absorption coefficient	0.078 mm^-1
F(000)	350
Crystal size	0.47 x 0.23 x 0.10 mm
Theta range for data collection	2.20 to 27.71 deg.
Limiting indices	-7<=h<=7, -11<=k<=12, -21<=l<=21
Reflections collected / unique	10514 / 4019 [R(int) = 0.0275]
Completeness to theta = 27.71	97.6 %
Absorption correction	Multi-scan
Max. and min. transmission	0.9922 and 0.9641
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4019 / 0 / 220
Goodness-of-fit on F^2	1.037
Final R indices [I>2sigma(I)]	R1 = 0.0719, wR2 = 0.1891
R indices (all data)	R1 = 0.0906, wR2 = 0.2034

Largest diff. peak and hole 1.138 and -0.531 e.A^-3

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **A3**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
O(2)	-5081(3)	-2031(2)	10072(1)	23(1)
O(1)	5639(3)	538(2)	7291(1)	30(1)
C(8)	4920(5)	1975(2)	7158(2)	30(1)
C(5)	6701(5)	2650(3)	6656(2)	36(1)
C(4)	6620(6)	1859(3)	5811(2)	43(1)
C(6)	6361(6)	4277(3)	6625(2)	45(1)
C(2)	8445(5)	1529(3)	4485(2)	40(1)
C(3)	8552(6)	2352(3)	5297(2)	43(1)
C(7)	4116(7)	4731(3)	6212(2)	55(1)
C(1)	10373(5)	2011(3)	3968(2)	43(1)
C(12)	1346(4)	-2429(2)	8328(1)	18(1)
C(13)	3361(4)	-2816(2)	7960(1)	20(1)
C(10)	2154(4)	49(2)	8001(1)	23(1)
C(14)	4747(4)	-1807(2)	7624(1)	23(1)
C(9)	4152(4)	-368(2)	7640(1)	22(1)
C(11)	778(4)	-983(2)	8336(1)	22(1)
C(15)	-97(4)	-3537(2)	8693(1)	18(1)
C(16)	-1831(4)	-3236(2)	9179(1)	19(1)
C(17)	-3404(4)	-4166(2)	9585(1)	18(1)
C(18)	-3365(4)	-5675(2)	9554(1)	19(1)
C(19)	-5091(4)	-3504(2)	10046(1)	18(1)
C(21)	503(4)	-5006(2)	8491(1)	21(1)
N(1)	1015(4)	-6157(2)	8316(1)	29(1)
C(20)	-6827(4)	-1331(2)	10500(1)	23(1)

Table S3. Bond length (Å) and angles (deg.) for **A3**.

O(2)-C(19)	1.363(2)
O(2)-C(20)	1.423(2)
O(1)-C(9)	1.357(3)
O(1)-C(8)	1.440(3)
C(8)-C(5)	1.503(3)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(5)-C(4)	1.528(4)
C(5)-C(6)	1.534(4)
C(5)-H(5)	1.0000
C(4)-C(3)	1.519(4)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(6)-C(7)	1.511(5)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(2)-C(3)	1.492(4)
C(2)-C(1)	1.516(4)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(1)-H(1A)	0.9800
C(1)-H(1B)	0.9800
C(1)-H(1C)	0.9800
C(12)-C(11)	1.394(3)
C(12)-C(13)	1.396(3)
C(12)-C(15)	1.479(3)
C(13)-C(14)	1.373(3)
C(13)-H(13)	0.9500
C(10)-C(11)	1.384(3)
C(10)-C(9)	1.389(3)
C(10)-H(10)	0.9500
C(14)-C(9)	1.391(3)
C(14)-H(14)	0.9500
C(11)-H(11)	0.9500
C(15)-C(16)	1.350(3)
C(15)-C(21)	1.442(3)
C(16)-C(17)	1.452(3)
C(16)-H(16)	0.9500
C(17)-C(18)	1.398(3)
C(17)-C(19)	1.411(3)
C(18)-C(19)#1	1.377(3)
C(18)-H(18)	0.9500
C(19)-C(18)#1	1.377(3)
C(21)-N(1)	1.143(3)
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800

C(19)-O(2)-C(20)	117.79(16)
C(9)-O(1)-C(8)	118.09(18)
O(1)-C(8)-C(5)	106.66(19)
O(1)-C(8)-H(8A)	110.4
C(5)-C(8)-H(8A)	110.4
O(1)-C(8)-H(8B)	110.4
C(5)-C(8)-H(8B)	110.4
H(8A)-C(8)-H(8B)	108.6
C(8)-C(5)-C(4)	110.2(2)
C(8)-C(5)-C(6)	110.4(2)
C(4)-C(5)-C(6)	112.7(2)
C(8)-C(5)-H(5)	107.8
C(4)-C(5)-H(5)	107.8
C(6)-C(5)-H(5)	107.8
C(3)-C(4)-C(5)	113.8(2)
C(3)-C(4)-H(4A)	108.8
C(5)-C(4)-H(4A)	108.8
C(3)-C(4)-H(4B)	108.8
C(5)-C(4)-H(4B)	108.8
H(4A)-C(4)-H(4B)	107.7
C(7)-C(6)-C(5)	117.6(3)
C(7)-C(6)-H(6A)	107.9
C(5)-C(6)-H(6A)	107.9
C(7)-C(6)-H(6B)	107.9
C(5)-C(6)-H(6B)	107.9
H(6A)-C(6)-H(6B)	107.2
C(3)-C(2)-C(1)	112.5(3)
C(3)-C(2)-H(2A)	109.1
C(1)-C(2)-H(2A)	109.1
C(3)-C(2)-H(2B)	109.1
C(1)-C(2)-H(2B)	109.1
H(2A)-C(2)-H(2B)	107.8
C(2)-C(3)-C(4)	112.2(3)
C(2)-C(3)-H(3A)	109.2
C(4)-C(3)-H(3A)	109.2
C(2)-C(3)-H(3B)	109.2
C(4)-C(3)-H(3B)	109.2
H(3A)-C(3)-H(3B)	107.9
C(6)-C(7)-H(7A)	109.5
C(6)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(6)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(2)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	109.5
C(2)-C(1)-H(1C)	109.5
H(1A)-C(1)-H(1C)	109.5
H(1B)-C(1)-H(1C)	109.5
C(11)-C(12)-C(13)	117.57(19)
C(11)-C(12)-C(15)	122.42(18)
C(13)-C(12)-C(15)	120.02(18)
C(14)-C(13)-C(12)	121.3(2)
C(14)-C(13)-H(13)	119.4
C(12)-C(13)-H(13)	119.4
C(11)-C(10)-C(9)	119.14(19)

C(11)-C(10)-H(10)	120.4
C(9)-C(10)-H(10)	120.4
C(13)-C(14)-C(9)	120.2(2)
C(13)-C(14)-H(14)	119.9
C(9)-C(14)-H(14)	119.9
O(1)-C(9)-C(10)	124.7(2)
O(1)-C(9)-C(14)	115.46(19)
C(10)-C(9)-C(14)	119.81(19)
C(10)-C(11)-C(12)	122.0(2)
C(10)-C(11)-H(11)	119.0
C(12)-C(11)-H(11)	119.0
C(16)-C(15)-C(21)	121.50(19)
C(16)-C(15)-C(12)	124.21(18)
C(21)-C(15)-C(12)	114.29(17)
C(15)-C(16)-C(17)	131.75(19)
C(15)-C(16)-H(16)	114.1
C(17)-C(16)-H(16)	114.1
C(18)-C(17)-C(19)	117.48(19)
C(18)-C(17)-C(16)	124.65(18)
C(19)-C(17)-C(16)	117.87(18)
C(19)#1-C(18)-C(17)	121.79(19)
C(19)#1-C(18)-H(18)	119.1
C(17)-C(18)-H(18)	119.1
O(2)-C(19)-C(18)#1	122.98(18)
O(2)-C(19)-C(17)	116.29(18)
C(18)#1-C(19)-C(17)	120.72(18)
N(1)-C(21)-C(15)	178.2(2)
O(2)-C(20)-H(20A)	109.5
O(2)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
O(2)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5

Symmetry transformations used to generate equivalent atoms:
#1 -x-1,-y-1,-z+2

Table S4. Anisotropic displacement parameters ($Å^2$ x10^3) for **A3**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U11 + ... + 2 h k a^* b^* U12]$.

	U11	U22	U33	U23	U13	U12
O(2)	30(1)	10(1)	31(1)	2(1)	16(1)	3(1)
O(1)	32(1)	19(1)	42(1)	7(1)	18(1)	-1(1)
C(8)	36(1)	19(1)	36(1)	3(1)	14(1)	4(1)
C(5)	41(2)	25(1)	45(2)	5(1)	19(1)	1(1)
C(4)	57(2)	30(1)	44(2)	6(1)	16(1)	2(1)
C(6)	63(2)	24(1)	53(2)	6(1)	30(2)	5(1)
C(2)	37(2)	35(1)	48(2)	10(1)	8(1)	4(1)
C(3)	59(2)	30(1)	44(2)	6(1)	17(1)	7(1)
C(7)	95(3)	29(2)	41(2)	2(1)	12(2)	9(2)
C(1)	42(2)	51(2)	36(2)	3(1)	7(1)	1(1)
C(12)	21(1)	14(1)	19(1)	1(1)	3(1)	1(1)
C(13)	23(1)	15(1)	24(1)	2(1)	6(1)	2(1)
C(10)	30(1)	13(1)	26(1)	2(1)	7(1)	2(1)
C(14)	22(1)	21(1)	28(1)	3(1)	8(1)	2(1)
C(9)	24(1)	19(1)	25(1)	3(1)	6(1)	-3(1)
C(11)	24(1)	17(1)	26(1)	2(1)	8(1)	4(1)
C(15)	22(1)	13(1)	20(1)	1(1)	3(1)	1(1)
C(16)	22(1)	13(1)	22(1)	2(1)	4(1)	2(1)
C(17)	21(1)	15(1)	18(1)	3(1)	4(1)	2(1)
C(18)	22(1)	14(1)	22(1)	1(1)	7(1)	4(1)
C(19)	24(1)	11(1)	21(1)	2(1)	5(1)	2(1)
C(21)	24(1)	17(1)	23(1)	3(1)	9(1)	0(1)
N(1)	34(1)	17(1)	38(1)	1(1)	16(1)	2(1)
C(20)	30(1)	12(1)	29(1)	-1(1)	13(1)	4(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **A3**.

	x	y	z	U(eq)
H(8A)	4852	2549	7683	35
H(8B)	3359	1934	6865	35
H(5)	8274	2530	6931	44
H(4A)	6722	809	5873	51
H(4B)	5100	2007	5521	51
H(6A)	6486	4716	7191	54
H(6B)	7668	4700	6345	54
H(2A)	6920	1661	4193	47
H(2B)	8560	485	4564	47
H(3A)	8430	3395	5219	52
H(3B)	10078	2223	5589	52
H(7A)	3976	4335	5645	82
H(7B)	4122	5790	6230	82
H(7C)	2795	4364	6495	82
H(1A)	10235	3035	3871	64
H(1B)	10242	1432	3446	64
H(1C)	11888	1876	4252	64
H(13)	3782	-3796	7941	24
H(10)	1739	1030	8018	27
H(14)	6118	-2092	7380	28
H(11)	-595	-697	8578	26
H(16)	-2064	-2232	9273	23
H(18)	-2243	-6147	9248	23
H(20A)	-8369	-1677	10260	35
H(20B)	-6638	-283	10464	35
H(20C)	-6675	-1552	11073	35