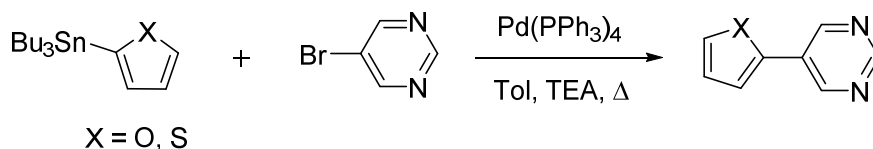


Supplementary Materials: A Raman Spectroscopic and Computational Study of New Aromatic Pyrimidine-Based Halogen Bond Acceptors

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General Summary

Reagents and solvents were purchased from commercial sources and used without further purification unless otherwise specified. DMF was degassed in 20 L drums and passed through two sequential purification columns (activated alumina; molecular sieves for DMF) under a positive argon atmosphere. Thin layer chromatography (TLC) was performed on SiO₂-60 F254 aluminum plates with visualization by UV light or staining. Flash column chromatography was performed using Purasil SiO₂-60, 230–400 mesh from Fisher. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance-300 (300 MHz), Bruker Avance DRX-500 (500 MHz spectrometer and are reported in ppm using solvent as an internal standard (CDCl₃ at 7.26 ppm). Data reported as: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, b = broad, ap = apparent; coupling constant(s) in Hz; integration.



Scheme S1. Synthesis of pyrimidine halogen bond acceptors.

Synthesis of PrmT

To a flame dried round bottom flask (RBF) equipped with a stir bar, 1 equivalence (9.43 mmol, 1.51 g) of 5-bromopyrimidine was added followed by 0.05 equivalence (0.47 mmol, 0.53 g) of Pd(PPh₃)₄. The RBF was then put under an inert atmosphere of N₂. The solid reagents were then dissolved in dry toluene (47 mL) after which 1.1 equivalence (10.37 mmol, 3.30 mL) of 2-(tributylstannyl)thiophene and 1.31 mL of trimethylamine (TEA) were added. The reaction was allowed to run for 12 h at the reflux. After 12 h, the reaction mixture was cooled to room temperature and 100 mL of NaHCO₃ was added to quench the reaction. Ethyl acetate was used to extract the compound and the organic layer was then washed with 100 mL of DI water three times. The organic layer was then separated and dried over Na₂SO₄. The organic solvent was then removed by rotary evaporation to afford a yellow solid. The compound was then purified by column chromatography using silica gel as the stationary phase and a 1:1 mixture of hexanes and ethyl acetate (3% TEA) as the mobile phase to afford 1.51 g (99.6% yield) of pure 5-(thiophen-2-yl)pyrimidine pale beige solid. ¹H NMR (300 MHz, CDCl₃) δ = 9.12, 8.96, 7.44, 7.17.

Synthesis of PrmF

To a flame dried RBF equipped with a stir bar, 1 equivalence (6.29 mmol, 1.01 g) of 5-bromopyrimidine was added followed by 0.1 equivalence (0.63 mmol, 0.73 g) of Pd(PPh₃)₄. The RBF was then put under an inert atmosphere of N₂. The solid reagents were then dissolved in dry toluene (30 mL) after which 1.2 equivalence (7.55 mmol, 2.38 mL) of 2-(tributylstannyl)furan and 0.5 mL of trimethylamine were added. The reaction was allowed to run for 8 hours at the reflux. After 8 h, the reaction mixture was cooled to room temperature and 100 mL of NaHCO₃ was added to quench the reaction. Ethyl acetate was used to extract the compound and the organic layer was then washed with

100 mL of DI water three times. The organic layer was then separated and dried over Na_2SO_4 . The organic solvent was then removed by rotary evaporation to afford a brown solid. The compound was then purified by column chromatography using silica gel as the stationary phase and a 1:1 mixture of hexanes and ethyl acetate as the mobile phase to afford 0.87 g (95% yield) of pure 5-(furan-2-yl)pyrimidine pale yellow solid. ^1H NMR (300 MHz, CDCl_3) δ = 8.85, 8.73, 7.32, 6.57, 6.28.

Synthesis of $(\text{NO}_2)_2\text{BAI}$

The synthesis of the halogen bond donors $((\text{NO}_2)_2\text{BAI})$ was reported in a previous work.¹

NMR Analysis

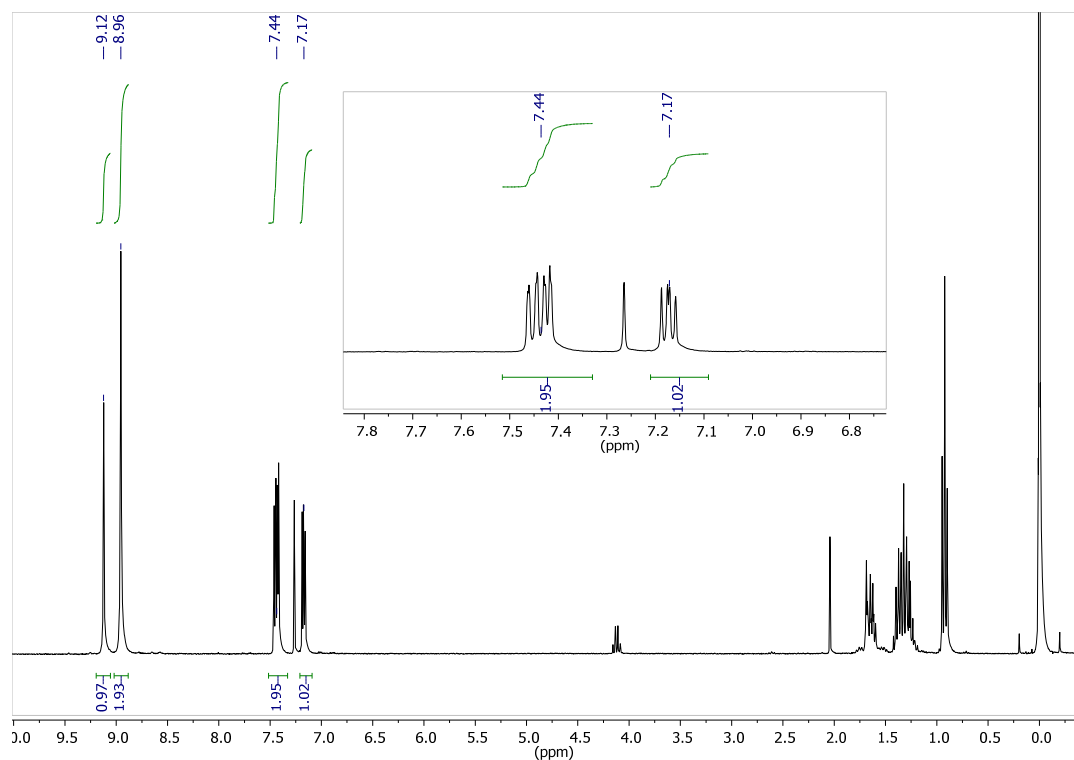


Figure S1. ^1H NMR of 5-(thiophen-2-yl)pyrimidine (ethyl acetate and tributyltin bromide impurities).

¹ Nguyen, S. T.; Rheingold, A. L.; Tschumper, G. S.; Watkins, D.L. Elucidating the Effects of Fluoro and Nitro Substituents on HalogenBond Driven Assemblies of Pyridyl-Capped π -Conjugated Molecules. *Cryst. Growth Des.* 2016, 16, 6648–6653

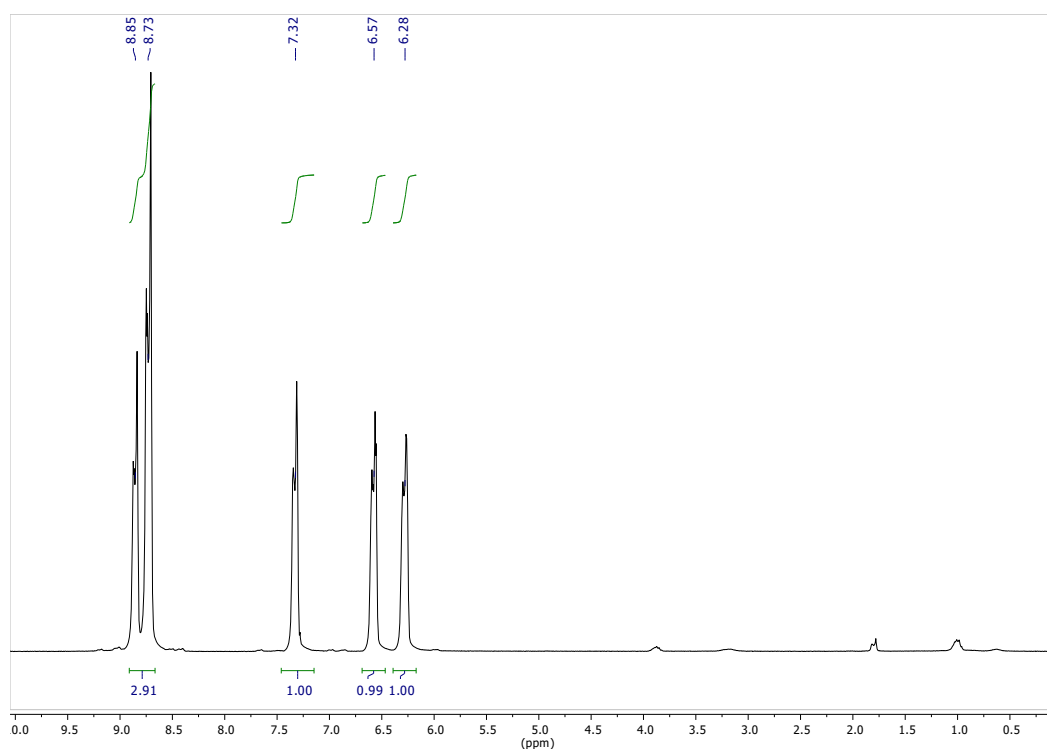


Figure S2. ^1H NMR of 5-(furan-2-yl)pyrimidine.

Crystal Data and Structure Refinement

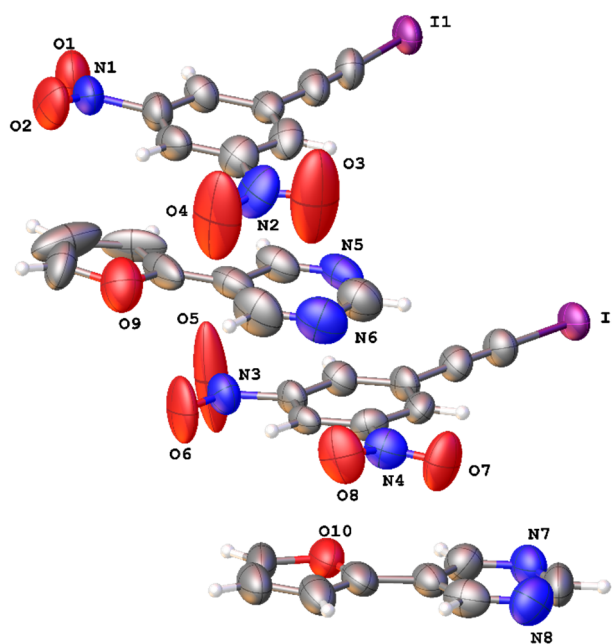


Table S1. Crystal data and structure refinement for dwat21_0m_a_sq. (**PrmF** and (**NO**)₂**BAI**).

Identification Code	dwat21_0m_a_sq
Empirical formula	C ₁₆ H ₉ I N ₄ O ₅
Formula weight	464.17
Temperature	100 K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1

Unit cell dimensions	$a = 6.9398(10) \text{ \AA}$	$\alpha = 79.340(4)^\circ$
	$b = 16.126(2) \text{ \AA}$	$\beta = 80.010(4)^\circ$
	$c = 18.517(3) \text{ \AA}$	$\gamma = 89.242(4)^\circ$
Volume	2005.2(5) \AA^3	
Z	4	
Density (calculated)	1.538 Mg/m^3	
Absorption coefficient	1.628 mm^{-1}	
F(000)	904	
Crystal size	$0.3 \times 0.2 \times 0.12 \text{ mm}^3$	
Theta range for data collection	1.550 to 26.452°	
Index ranges	$-8 \leq h \leq 8, -15 \leq k \leq 20, -23 \leq l \leq 23$	
Reflections collected	22950	
Independent reflections	8062 [R(int) = 0.0516]	
Completeness to $\theta = 25.242^\circ$	98.9%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7454 and 0.5187	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8062/0/469	
Goodness-of-fit on F^2	1.043	
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0484, wR2 = 0.1119	
R indices (all data)	R1 = 0.0672, wR2 = 0.1220	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.026 and $-1.860 \text{ e.\AA}^{-3}$	
Squeeze	151e/uc; two furanylpurimidine	

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for dwt21_0m_a_sq. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
I(2)	4554(1)	6701(1)	197(1)	23(1)
I(1)	413(1)	1758(1)	78(1)	23(1)
O(10)	10904(5)	6773(2)	3171(2)	32(1)
O(7)	5646(7)	8646(2)	3544(2)	39(1)
O(8)	5728(6)	7904(3)	4639(2)	40(1)
O(1)	1968(6)	−67(2)	3945(2)	36(1)
O(2)	1744(7)	641(3)	4846(2)	41(1)
O(6)	7237(7)	4956(3)	4851(2)	45(1)
O(9)	6773(6)	1941(3)	3760(2)	40(1)
N(3)	6990(7)	4960(3)	4219(2)	26(1)
N(4)	5751(7)	7974(3)	3962(2)	27(1)
N(5)	6063(6)	3278(3)	1258(2)	28(1)
N(1)	1822(7)	587(3)	4185(2)	29(1)
N(7)	10064(7)	8584(3)	1327(2)	28(1)
N(2)	1997(8)	3678(3)	3615(3)	36(1)
C(14)	6333(7)	6460(3)	4097(3)	18(1)
C(9)	5036(8)	6627(3)	1253(3)	23(1)
N(8)	9809(7)	9641(3)	2081(3)	35(1)
C(15)	5913(7)	7201(3)	3648(3)	20(1)
C(13)	6483(7)	5749(3)	3766(3)	19(1)
C(11)	5729(7)	6521(3)	2617(3)	20(1)
C(16)	5626(7)	7252(3)	2917(3)	20(1)
C(1)	870(8)	1962(3)	1083(3)	23(1)
N(6)	6341(8)	4136(3)	2149(3)	38(1)

C(29)	10381(8)	8207(3)	2605(3)	24(1)
C(4)	1523(7)	1345(3)	2937(3)	22(1)
C(10)	5348(7)	6560(3)	1878(3)	22(1)
C(3)	1400(7)	2099(3)	2424(3)	21(1)
C(30)	10339(8)	7997(3)	1913(3)	27(1)
C(27)	10852(8)	7652(4)	3958(3)	32(1)
C(2)	1125(8)	2052(3)	1686(3)	24(1)
C(5)	1755(8)	1392(3)	3651(3)	24(1)
O(3)	1654(11)	4320(3)	3209(3)	87(2)
C(21)	6551(8)	2628(4)	2479(3)	26(1)
O(4)	2503(10)	3688(3)	4195(3)	79(2)
C(12)	6176(7)	5755(3)	3044(3)	21(1)
O(5)	7200(11)	4339(3)	3943(3)	93(2)
C(7)	1795(8)	2866(3)	3381(3)	27(1)
C(8)	1533(8)	2870(3)	2655(3)	25(1)
C(26)	11180(8)	6829(4)	4338(3)	34(1)
C(22)	6297(8)	2583(4)	1757(3)	26(1)
C(6)	1896(8)	2135(3)	3893(3)	26(1)
C(20)	6703(8)	1872(4)	3037(3)	34(1)
C(28)	10694(8)	7593(4)	3253(3)	28(1)
C(32)	10081(8)	9042(4)	2655(3)	29(1)
C(19)	6720(8)	1091(4)	2958(3)	36(2)
C(25)	11211(8)	6322(4)	3851(3)	36(2)
C(17)	6831(8)	1117(3)	4147(3)	33(1)
C(31)	9820(8)	9372(3)	1443(3)	31(1)
C(23)	6081(9)	4016(4)	1486(3)	34(1)
C(24)	6584(9)	3433(4)	2640(3)	38(2)
C(18)	6815(9)	591(4)	3680(4)	52(2)

Table S3. Bond lengths [Å] and angles [°] for dwat21_0m_a_sq.

Bond lengths		Angles	
I(2)–C(9)	2.023(5)	C(28)–O(10)–C(25)	106.5(5)
I(1)–C(1)	2.026(5)	C(20)–O(9)–C(17)	105.6(5)
O(10)–C(28)	1.363(7)	O(6)–N(3)–C(13)	119.3(4)
O(10)–C(25)	1.382(6)	O(5)–N(3)–O(6)	121.9(5)
O(7)–N(4)	1.218(6)	O(5)–N(3)–C(13)	118.7(4)
O(8)–N(4)	1.235(5)	O(7)–N(4)–O(8)	123.9(4)
O(1)–N(1)	1.215(6)	O(7)–N(4)–C(15)	118.5(4)
O(2)–N(1)	1.234(6)	O(8)–N(4)–C(15)	117.6(4)
O(6)–N(3)	1.211(5)	C(23)–N(5)–C(22)	116.8(5)
O(9)–C(20)	1.372(6)	O(1)–N(1)–O(2)	125.1(5)
O(9)–C(17)	1.392(6)	O(1)–N(1)–C(5)	118.4(4)
N(3)–C(13)	1.462(6)	O(2)–N(1)–C(5)	116.5(5)
N(3)–O(5)	1.202(6)	C(31)–N(7)–C(30)	116.7(5)
N(4)–C(15)	1.465(6)	O(3)–N(2)–C(7)	118.9(5)
N(5)–C(22)	1.341(7)	O(4)–N(2)–O(3)	121.8(5)
N(5)–C(23)	1.336(7)	O(4)–N(2)–C(7)	119.4(5)
N(1)–C(5)	1.486(6)	C(15)–C(14)–H(14)	122.2
N(7)–C(30)	1.341(7)	C(15)–C(14)–C(13)	115.6(4)
N(7)–C(31)	1.330(7)	C(13)–C(14)–H(14)	122.2
N(2)–O(3)	1.209(6)	C(10)–C(9)–I(2)	178.0(5)
N(2)–O(4)	1.189(6)	C(31)–N(8)–C(32)	114.9(5)

N(2)–C(7)	1.470(7)	C(14)–C(15)–N(4)	118.2(4)
C(14)–H(14)	0.9500	C(14)–C(15)–C(16)	123.6(4)
C(14)–C(15)	1.382(7)	C(16)–C(15)–N(4)	118.2(4)
C(14)–C(13)	1.391(7)	C(14)–C(13)–N(3)	116.9(4)
C(9)–C(10)	1.199(7)	C(12)–C(13)–N(3)	119.5(4)
N(8)–C(32)	1.336(7)	C(12)–C(13)–C(14)	123.6(4)
N(8)–C(31)	1.330(7)	C(16)–C(11)–C(10)	119.3(4)
C(15)–C(16)	1.389(7)	C(16)–C(11)–C(12)	119.8(4)
C(13)–C(12)	1.390(6)	C(12)–C(11)–C(10)	120.9(4)
C(11)–C(16)	1.390(7)	C(15)–C(16)–C(11)	119.0(4)
C(11)–C(10)	1.427(6)	C(15)–C(16)–H(16)	120.5
C(11)–C(12)	1.400(7)	C(11)–C(16)–H(16)	120.5
C(16)–H(16)	0.9500	C(2)–C(1)–I(1)	177.6(5)
C(1)–C(2)	1.195(7)	C(23)–N(6)–C(24)	115.5(5)
N(6)–C(23)	1.322(7)	C(30)–C(29)–C(28)	123.1(5)
N(6)–C(24)	1.343(8)	C(32)–C(29)–C(30)	116.3(5)
C(29)–C(30)	1.390(7)	C(32)–C(29)–C(28)	120.6(5)
C(29)–C(28)	1.453(7)	C(3)–C(4)–H(4)	120.5
C(29)–C(32)	1.376(8)	C(5)–C(4)–H(4)	120.5
C(4)–H(4)	0.9500	C(5)–C(4)–C(3)	118.9(5)
C(4)–C(3)	1.410(7)	C(9)–C(10)–C(11)	177.5(5)
C(4)–C(5)	1.374(7)	C(4)–C(3)–C(2)	119.1(5)
C(3)–C(2)	1.427(7)	C(8)–C(3)–C(4)	118.9(5)
C(3)–C(8)	1.397(7)	C(8)–C(3)–C(2)	122.0(5)
C(30)–H(30)	0.9500	N(7)–C(30)–C(29)	121.3(5)
C(27)–H(27)	0.9500	N(7)–C(30)–H(30)	119.3
C(27)–C(26)	1.419(8)	C(29)–C(30)–H(30)	119.3
C(27)–C(28)	1.349(8)	C(26)–C(27)–H(27)	126.3
C(5)–C(6)	1.366(7)	C(28)–C(27)–H(27)	126.3
C(21)–C(22)	1.393(7)	C(28)–C(27)–C(26)	107.4(6)
C(21)–C(20)	1.459(8)	C(1)–C(2)–C(3)	176.1(6)
C(21)–C(24)	1.387(8)	C(4)–C(5)–N(1)	117.7(5)
C(12)–H(12)	0.9500	C(6)–C(5)–N(1)	118.7(5)
C(7)–C(8)	1.386(7)	C(6)–C(5)–C(4)	123.6(5)
C(7)–C(6)	1.379(7)	C(22)–C(21)–C(20)	122.0(5)
C(8)–H(8)	0.9500	C(24)–C(21)–C(22)	115.6(5)
C(26)–H(26)	0.9500	C(24)–C(21)–C(20)	122.3(5)
C(26)–C(25)	1.322(9)	C(13)–C(12)–C(11)	118.4(5)
C(22)–H(22)	0.9500	C(13)–C(12)–H(12)	120.8
C(6)–H(6)	0.9500	C(11)–C(12)–H(12)	120.8
C(20)–C(19)	1.294(8)	C(8)–C(7)–N(2)	118.6(5)
C(32)–H(32)	0.9500	C(6)–C(7)–N(2)	118.2(5)
C(19)–H(19)	0.9500	C(6)–C(7)–C(8)	123.2(5)
C(19)–C(18)	1.440(9)	C(3)–C(8)–H(8)	120.6
C(25)–H(25)	0.9500	C(7)–C(8)–C(3)	118.8(5)
C(17)–H(17)	0.9500	C(7)–C(8)–H(8)	120.6
C(17)–C(18)	1.318(9)	C(27)–C(26)–H(26)	126.7
C(31)–H(31)	0.9500	C(25)–C(26)–C(27)	106.6(5)
C(23)–H(23)	0.9500	C(25)–C(26)–H(26)	126.7
C(24)–H(24)	0.9500	N(5)–C(22)–C(21)	121.8(5)
C(18)–H(18)	0.9500	N(5)–C(22)–H(22)	119.1
		C(21)–C(22)–H(22)	119.1

C(5)–C(6)–C(7)	116.7(5)
C(5)–C(6)–H(6)	121.7
C(7)–C(6)–H(6)	121.7
O(9)–C(20)–C(21)	120.1(5)
C(19)–C(20)–O(9)	111.4(5)
C(19)–C(20)–C(21)	128.5(5)
O(10)–C(28)–C(29)	117.5(5)
C(27)–C(28)–O(10)	109.1(5)
C(27)–C(28)–C(29)	133.4(6)
N(8)–C(32)–C(29)	123.7(5)
N(8)–C(32)–H(32)	118.1
C(29)–C(32)–H(32)	118.1
C(20)–C(19)–H(19)	126.7
C(20)–C(19)–C(18)	106.5(5)
C(18)–C(19)–H(19)	126.7
O(10)–C(25)–H(25)	124.8
C(26)–C(25)–O(10)	110.4(5)
C(26)–C(25)–H(25)	124.8
O(9)–C(17)–H(17)	125.5
C(18)–C(17)–O(9)	109.0(6)
C(18)–C(17)–H(17)	125.5
N(7)–C(31)–H(31)	116.5
N(8)–C(31)–N(7)	127.0(5)
N(8)–C(31)–H(31)	116.5
N(5)–C(23)–H(23)	116.6
N(6)–C(23)–N(5)	126.8(6)
N(6)–C(23)–H(23)	116.6
N(6)–C(24)–C(21)	123.5(5)
N(6)–C(24)–H(24)	118.2
C(21)–C(24)–H(24)	118.2
C(19)–C(18)–H(18)	126.3
C(17)–C(18)–C(19)	107.4(6)
C(17)–C(18)–H(18)	126.3

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for dwat21_0m_a_sq. The anisotropic displacement factor exponent takes the form: $-2^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$.

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
I(2)	26(1)	31(1)	12(1)	−3(1)	−6(1)	−1(1)
I(1)	26(1)	29(1)	13(1)	0(1)	−6(1)	1(1)
O(10)	27(2)	38(2)	26(2)	5(2)	−5(2)	−2(2)
O(7)	69(3)	19(2)	29(2)	−4(2)	−9(2)	2(2)
O(8)	58(3)	43(2)	26(2)	−18(2)	−14(2)	10(2)
O(1)	47(3)	30(2)	31(2)	1(2)	−15(2)	4(2)
O(2)	58(3)	46(3)	18(2)	3(2)	−16(2)	−7(2)
O(6)	79(3)	42(2)	17(2)	−2(2)	−22(2)	13(2)
O(9)	49(3)	43(3)	27(2)	−4(2)	−6(2)	7(2)
N(3)	31(3)	30(3)	19(2)	−2(2)	−9(2)	1(2)
N(4)	29(3)	32(3)	23(2)	−12(2)	−3(2)	2(2)
N(5)	20(3)	49(3)	19(2)	−11(2)	−4(2)	2(2)
N(1)	30(3)	34(3)	22(2)	6(2)	−11(2)	−3(2)
N(7)	30(3)	35(3)	19(2)	−3(2)	−6(2)	0(2)

N(2)	53(4)	37(3)	17(2)	−6(2)	2(2)	−3(2)
C(14)	14(3)	28(3)	11(2)	−4(2)	−3(2)	−2(2)
C(9)	27(3)	28(3)	16(3)	−4(2)	−5(2)	−1(2)
N(8)	41(3)	28(3)	35(3)	−6(2)	−2(2)	3(2)
C(15)	21(3)	21(3)	19(2)	−9(2)	−2(2)	−2(2)
C(13)	22(3)	25(3)	12(2)	−3(2)	−6(2)	0(2)
C(11)	22(3)	26(3)	11(2)	−2(2)	−5(2)	0(2)
C(16)	18(3)	24(3)	16(2)	1(2)	−1(2)	−2(2)
C(1)	27(3)	24(3)	16(3)	0(2)	−4(2)	4(2)
N(6)	42(3)	44(3)	36(3)	−19(2)	−11(2)	0(2)
C(29)	19(3)	33(3)	20(3)	−2(2)	−3(2)	0(2)
C(4)	22(3)	28(3)	17(2)	−6(2)	−5(2)	4(2)
C(10)	21(3)	27(3)	15(2)	−2(2)	−1(2)	1(2)
C(3)	17(3)	30(3)	14(2)	−1(2)	−1(2)	−1(2)
C(30)	28(3)	27(3)	26(3)	−3(2)	−4(2)	−1(2)
C(27)	21(3)	46(4)	25(3)	4(3)	−4(2)	3(3)
C(2)	20(3)	31(3)	18(3)	1(2)	−2(2)	3(2)
C(5)	25(3)	27(3)	19(3)	1(2)	−6(2)	2(2)
O(3)	184(7)	34(3)	56(3)	−12(3)	−53(4)	7(3)
C(21)	17(3)	44(3)	19(3)	−10(2)	−4(2)	0(2)
O(4)	169(6)	48(3)	38(3)	−17(2)	−55(4)	−1(3)
C(12)	20(3)	27(3)	17(2)	−6(2)	−3(2)	2(2)
O(5)	226(8)	32(3)	50(3)	−25(2)	−85(4)	50(4)
C(7)	29(3)	33(3)	19(3)	−8(2)	0(2)	2(2)
C(8)	25(3)	31(3)	16(3)	−2(2)	2(2)	4(2)
C(26)	28(3)	46(4)	24(3)	6(3)	−7(2)	−1(3)
C(22)	21(3)	43(3)	19(3)	−14(2)	−4(2)	2(2)
C(6)	24(3)	37(3)	16(3)	−1(2)	−6(2)	−5(2)
C(20)	22(3)	65(4)	13(3)	−2(3)	−5(2)	−4(3)
C(28)	19(3)	38(3)	27(3)	0(2)	−6(2)	0(2)
C(32)	26(3)	40(3)	22(3)	−14(2)	−1(2)	−2(2)
C(19)	25(3)	60(4)	33(3)	−38(3)	4(3)	−13(3)
C(25)	21(3)	43(4)	34(3)	18(3)	−6(3)	0(3)
C(17)	36(4)	31(3)	24(3)	7(2)	1(3)	4(3)
C(31)	29(3)	32(3)	27(3)	8(2)	−6(2)	4(2)
C(23)	34(4)	40(3)	30(3)	−11(3)	−9(3)	1(3)
C(24)	43(4)	53(4)	25(3)	−18(3)	−11(3)	3(3)
C(18)	34(4)	35(4)	84(6)	−22(4)	13(4)	−12(3)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for dwat21_0m_a_sq.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U(eq)</i>
H(14)	6508	6438	4598	21
H(16)	5364	7778	2628	24
H(4)	1447	812	2793	26
H(30)	10509	7427	1854	33
H(27)	10760	8153	4162	39
H(12)	6266	5251	2844	25
H(8)	1446	3387	2321	30
H(26)	11345	6673	4844	41

H(22)	6290	2047	1615	32
H(6)	2055	2148	4391	31
H(32)	10067	9201	3125	35
H(19)	6678	887	2511	43
H(25)	11416	5731	3954	43
H(17)	6875	958	4664	39
H(31)	9633	9786	1026	37
H(23)	5887	4505	1134	40
H(24)	6789	3491	3122	46
H(18)	6859	−7	3799	63

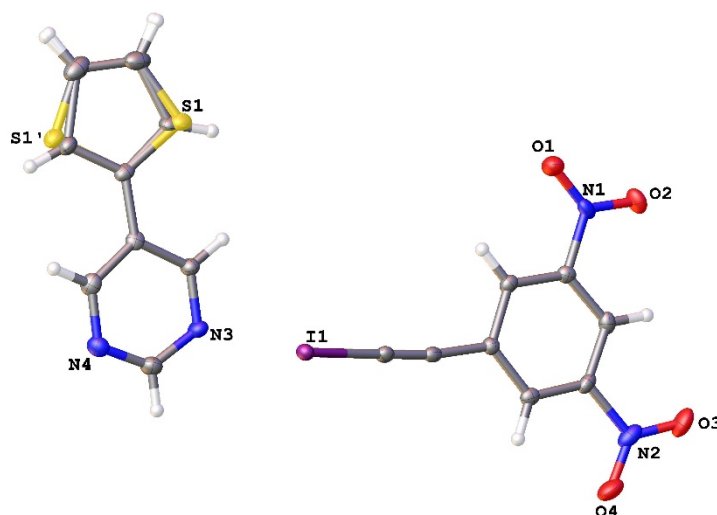


Table S6. Crystal data and structure refinement for dwat16_0m_a. (**PrmT** and **(NO₂)₂BAI**).

Identification Code	SN121616-TH	
Empirical formula	C ₃₂ H ₁₈ I ₂ N ₈ O ₈ S ₂	
Formula weight	960.46	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	$a = 9.2195(6)$ Å	$\alpha = 90^\circ$
	$b = 5.7344(4)$ Å	$\beta = 93.209(3)^\circ$
	$c = 32.1204(16)$ Å	$\gamma = 90^\circ$
Volume	1695.49(18) Å ³	
Z	2	
Density (calculated)	1.881 Mg/m ³	
Absorption coefficient	2.043 mm ^{−1}	
F(000)	936	
Crystal size	0.31 × 0.29 × 0.08 mm ³	
Theta range for data collection	2.267 to 28.339°	
Index ranges	−12 ≤ h ≤ 12, −7 ≤ k ≤ 5, −42 ≤ l ≤ 42	
Reflections collected	14426	
Independent reflections	4232 [R(int) = 0.0722]	
Completeness to theta = 25.000°	99.9%	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.2627 and 0.1977	
Refinement method	Full-matrix least-squares on F ²	

Data / restraints / parameters	4232/30/242
Goodness-of-fit on F ²	1.164
Final R indices [I > 2sigma(I)]	R1 = 0.0438, wR2 = 0.1022
R indices (all data)	R1 = 0.0470, wR2 = 0.1040
Extinction coefficient	n/a
Largest diff. peak and hole	0.650 and −0.990 e.Å ^{−3}

Table S7. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for dwat16_0m_a. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
I(1)	8317(1)	2291(1)	5179(1)	16(1)
S(1')	6172(3)	−2085(5)	7255(1)	21(1)
O(2)	4257(3)	14818(5)	4030(1)	25(1)
O(4)	8878(3)	9484(5)	3079(1)	32(1)
O(1)	4173(3)	12806(5)	4601(1)	28(1)
O(3)	7742(4)	12817(5)	3032(1)	32(1)
N(3)	8766(3)	−573(6)	5890(1)	18(1)
N(4)	9385(3)	−3942(6)	6297(1)	21(1)
N(2)	8038(3)	10946(6)	3205(1)	24(1)
N(1)	4616(3)	13157(6)	4257(1)	19(1)
C(12)	7914(4)	176(6)	6187(1)	17(1)
C(1)	7830(3)	4667(6)	4729(1)	16(1)
C(11)	7726(4)	−1102(6)	6552(1)	15(1)
C(10)	8528(4)	−3172(7)	6588(1)	20(1)
C(7)	5688(3)	11503(6)	4097(1)	16(1)
C(13)	6715(4)	−356(6)	6863(1)	18(1)
C(9)	9450(4)	−2613(6)	5960(1)	21(1)
C(4)	7775(4)	8467(7)	3826(1)	16(1)
C(5)	7350(4)	10439(6)	3602(1)	18(1)
C(3)	7125(4)	8045(6)	4203(1)	15(1)
C(6)	6313(4)	12005(6)	3726(1)	18(1)
C(16)	4964(4)	1798(8)	7230(1)	28(1)
C(8)	6053(3)	9566(6)	4338(1)	16(1)
C(2)	7552(3)	6126(6)	4471(1)	16(1)
C(15)	5077(4)	−259(8)	7426(1)	30(1)
C(14')	5930(30)	1830(30)	6861(9)	21(1)
C(14)	6340(20)	−1750(40)	7192(6)	21(1)
S(1)	5965(10)	2244(9)	6849(3)	21(1)

Table S8. Bond lengths [\AA] and angles [$^\circ$] for dwat16_0m_a.

Bond lengths		Angles	
I(1)–C(1)	2.019(3)	C(15)–S(1')–C(13)	95.2(2)
S(1')–C(13)	1.700(4)	C(12)–N(3)–C(9)	116.7(3)
S(1')–C(15)	1.574(5)	C(9)–N(4)–C(10)	115.9(3)
O(2)–N(1)	1.234(4)	O(4)–N(2)–O(3)	125.2(3)
O(4)–N(2)	1.225(4)	O(4)–N(2)–C(5)	117.2(3)
O(1)–N(1)	1.218(4)	O(3)–N(2)–C(5)	117.6(3)
O(3)–N(2)	1.232(4)	O(2)–N(1)–C(7)	116.8(3)
N(3)–C(12)	1.340(4)	O(1)–N(1)–O(2)	124.9(3)
N(3)–C(9)	1.341(5)	O(1)–N(1)–C(7)	118.2(3)
N(4)–C(10)	1.333(5)	N(3)–C(12)–H(12)	118.9

N(4)–C(9)	1.329(5)	N(3)–C(12)–C(11)	122.2(3)
N(2)–C(5)	1.483(4)	C(11)–C(12)–H(12)	118.9
N(1)–C(7)	1.482(4)	C(2)–C(1)–I(1)	177.9(3)
C(12)–H(12)	0.9500	C(12)–C(11)–C(13)	122.0(3)
C(12)–C(11)	1.403(5)	C(10)–C(11)–C(12)	115.0(3)
C(1)–C(2)	1.194(5)	C(10)–C(11)–C(13)	122.9(3)
C(11)–C(10)	1.400(5)	N(4)–C(10)–C(11)	123.6(3)
C(11)–C(13)	1.467(4)	N(4)–C(10)–H(10)	118.2
C(10)–H(10)	0.9500	C(11)–C(10)–H(10)	118.2
C(7)–C(6)	1.383(5)	C(6)–C(7)–N(1)	118.9(3)
C(7)–C(8)	1.384(5)	C(6)–C(7)–C(8)	123.3(3)
C(13)–C(14')	1.45(2)	C(8)–C(7)–N(1)	117.8(3)
C(13)–C(14)	1.386(17)	C(11)–C(13)–S(1')	123.9(3)
C(13)–S(1)	1.643(8)	C(11)–C(13)–S(1)	121.9(4)
C(9)–H(9)	0.9500	C(14')–C(13)–S(1')	109.9(10)
C(4)–H(4)	0.9500	C(14')–C(13)–C(11)	125.9(11)
C(4)–C(5)	1.386(5)	C(14)–C(13)–C(11)	123.2(10)
C(4)–C(3)	1.402(4)	C(14)–C(13)–S(1)	114.9(10)
C(5)–C(6)	1.386(5)	N(3)–C(9)–H(9)	116.8
C(3)–C(8)	1.404(5)	N(4)–C(9)–N(3)	126.5(3)
C(3)–C(2)	1.438(5)	N(4)–C(9)–H(9)	116.8
C(6)–H(6)	0.9500	C(5)–C(4)–H(4)	121.0
C(16)–H(16)	0.9500	C(5)–C(4)–C(3)	118.0(3)
C(16)–H(16A)	0.9500	C(3)–C(4)–H(4)	121.0
C(16)–C(15)	1.339(6)	C(4)–C(5)–N(2)	119.0(3)
C(16)–C(14')	1.52(3)	C(4)–C(5)–C(6)	123.9(3)
C(16)–S(1)	1.593(9)	C(6)–C(5)–N(2)	117.1(3)
C(8)–H(8)	0.9500	C(4)–C(3)–C(8)	120.0(3)
C(15)–H(15)	0.9500	C(4)–C(3)–C(2)	122.2(3)
C(15)–H(15A)	0.9500	C(8)–C(3)–C(2)	117.7(3)
C(15)–C(14)	1.66(2)	C(7)–C(6)–C(5)	116.2(3)
C(14')–H(14')	0.9500	C(7)–C(6)–H(6)	121.9
C(14)–H(14)	0.9500	C(5)–C(6)–H(6)	121.9
		C(15)–C(16)–H(16)	125.0
		C(15)–C(16)–H(16A)	121.0
		C(15)–C(16)–C(14')	110.0(8)
		C(15)–C(16)–S(1)	118.0(4)
		C(14')–C(16)–H(16)	125.0
		S(1)–C(16)–H(16A)	121.0
		C(7)–C(8)–C(3)	118.7(3)
		C(7)–C(8)–H(8)	120.7
		C(3)–C(8)–H(8)	120.7
		C(1)–C(2)–C(3)	172.5(4)
		S(1')–C(15)–H(15)	121.4
		C(16)–C(15)–S(1')	117.2(3)
		C(16)–C(15)–H(15)	121.4
		C(16)–C(15)–H(15A)	126.9
		C(16)–C(15)–C(14)	106.3(7)
		C(14)–C(15)–H(15A)	126.9
		C(13)–C(14')–C(16)	107.6(14)
		C(13)–C(14')–H(14')	126.2
		C(16)–C(14')–H(14')	126.2

C(13)–C(14)–C(15)	105.1(14)
C(13)–C(14)–H(14)	127.4
C(15)–C(14)–H(14)	127.4
C(16)–S(1)–C(13)	95.5(4)

Symmetry transformations used to generate equivalent atoms:

Table S9. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for dwat16_0m_a. The anisotropic displacement factor exponent takes the form: $-2^2 [\text{h}^2 \text{a}^* \text{U}^{11} + \dots + 2 \text{h k a}^* \text{b}^* \text{U}^{12}]$.

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
I(1)	17(1)	15(1)	16(1)	0(1)	2(1)	2(1)
S(1')	24(1)	22(1)	18(1)	1(1)	5(1)	−2(1)
O(2)	24(1)	18(1)	31(1)	4(1)	−5(1)	6(1)
O(4)	34(2)	40(2)	25(1)	0(1)	13(1)	−4(1)
O(1)	30(2)	24(2)	32(2)	2(1)	12(1)	5(1)
O(3)	34(2)	38(2)	26(2)	13(1)	4(1)	−6(1)
N(3)	19(1)	22(2)	14(1)	0(1)	4(1)	2(1)
N(4)	20(1)	22(2)	22(2)	−1(1)	−2(1)	4(1)
N(2)	21(2)	36(2)	14(1)	1(1)	2(1)	−9(1)
N(1)	17(1)	12(2)	29(2)	−1(1)	0(1)	1(1)
C(12)	19(2)	18(2)	15(2)	−1(1)	2(1)	1(1)
C(1)	13(2)	18(2)	18(2)	−1(1)	2(1)	1(1)
C(11)	16(2)	17(2)	12(1)	−2(1)	−4(1)	−4(1)
C(10)	18(2)	25(2)	17(2)	3(1)	−4(1)	−1(2)
C(7)	13(2)	17(2)	17(2)	−2(1)	−1(1)	−1(1)
C(13)	18(2)	22(2)	13(1)	−4(1)	1(1)	−5(1)
C(9)	18(2)	23(2)	23(2)	−2(1)	2(1)	2(1)
C(4)	14(2)	19(2)	16(2)	−3(1)	0(1)	−3(1)
C(5)	20(2)	21(2)	15(2)	0(1)	3(1)	−7(1)
C(3)	16(2)	14(2)	15(2)	−1(1)	1(1)	−1(1)
C(6)	16(2)	16(2)	20(2)	3(1)	−4(1)	−3(1)
C(16)	25(2)	31(2)	30(2)	−12(1)	8(1)	−3(2)
C(8)	14(2)	19(2)	15(1)	0(1)	1(1)	−3(1)
C(2)	13(2)	16(2)	17(2)	−4(1)	3(1)	−1(1)
C(15)	31(2)	39(2)	21(2)	−5(1)	5(1)	−13(2)
C(14')	24(1)	21(2)	20(1)	−5(2)	6(1)	−1(2)
C(14)	24(1)	22(1)	18(1)	1(1)	5(1)	−2(1)
S(1)	24(1)	21(2)	20(1)	−5(2)	6(1)	−1(2)

Table S10. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for dwat16_0m_a.

	x	y	z	U(eq)
H(12)	7421	1621	6149	21
H(10)	8456	−4079	6834	24
H(9)	10038	−3163	5747	25
H(4)	8484	7434	3728	19
H(6)	6048	13346	3566	21
H(16)	4369	3056	7309	34
H(16A)	4306	2957	7315	34
H(8)	5588	9272	4589	19
H(15)	4520	−603	7658	36
H(15A)	4542	−762	7654	36

H(14')	5998	3054	6664	25
H(14)	6714	−3244	7266	25

Computational Results

Table S11. Cartesian coordinates (in Å) of the pyrimidine capped furan XB acceptor (**PrmF**) at the M06-2X/aug-cc-pVTZ level of theory.

	<i>x</i>	<i>y</i>	<i>z</i>
C	3.57825889	0.09741977	0.04859206
N	2.89882889	1.07808739	0.63763415
C	1.57876550	0.98429685	0.59747548
C	1.73873077	−1.03801133	−0.60273630
N	3.06326921	−0.95777709	−0.57066286
H	1.01905192	1.78073737	1.07595310
H	4.65848921	0.16812917	0.07787501
H	1.30774374	−1.89499573	−1.10551911
C	−0.53083405	−0.16009989	−0.05601063
C	−1.52346950	0.63341831	0.42579255
O	−1.06929135	−1.23494569	−0.68663473
C	−2.75310961	0.00292178	0.06654621
H	−1.39983318	1.55352342	0.96956850
C	−2.41392934	−1.12088128	−0.60333898
H	−3.75085304	0.34298100	0.27970623
H	−2.98355089	−1.90787997	−1.06303176
C	0.91817881	−0.07411190	−0.02198190

Table S12. Cartesian coordinates (in Å) of the pyrimidine capped thiophene XB acceptor (**PrmT**) at the M06-2X/aug-cc-pVTZ level of theory.

	<i>x</i>	<i>y</i>	<i>z</i>
C	3.63197307	0.19973830	0.16099702
N	2.87476650	1.24554445	0.47683448
C	1.56556581	1.08426914	0.34938590
C	1.89068252	−1.13136082	−0.37134679
N	3.20423443	−0.98308254	−0.26560481
H	0.94224721	1.94221447	0.57690176
H	4.70314799	0.32576068	0.25832266
H	1.53419673	−2.10231380	−0.70051310
C	−0.45930315	−0.27190863	−0.17879812
C	−1.43041961	0.37986915	0.52783548
S	−1.16416756	−1.38028333	−1.30040210
C	−2.74368323	−0.01729596	0.16680595
H	−1.21022344	1.10214653	1.30013991
C	−2.75136493	−0.96470183	−0.80860520
H	−3.64053767	0.37951115	0.61704450
H	−3.59950456	−1.44196497	−1.26929264
C	0.98883586	−0.11332982	−0.07047787

Table S13. Cartesian coordinates (in Å) of 1-(iodoethynyl)-3,5-dinitrobenzene (**(NO₂)₂BAI**) at the M06-2X/aug-cc-pVTZ level of theory.

	<i>x</i>	<i>y</i>	<i>z</i>
C	0.00000000	−1.20532835	1.34032941
C	0.00000000	−1.17312996	2.72030996
C	0.00000000	0.00000000	3.44833842
C	0.00000000	1.17312996	2.72030996
C	0.00000000	1.20532835	1.34032941
C	0.00000000	0.00000000	0.63613928
H	0.00000000	−2.15264409	0.82346156
H	0.00000000	0.00000000	4.52676740
H	0.00000000	2.15264409	0.82346156
I	0.00000000	0.00000000	−3.98192569
C	0.00000000	0.00000000	−0.79170376

C	0.00000000	0.00000000	−1.99345097
N	0.00000000	2.45635994	3.45746229
N	0.00000000	−2.45635994	3.45746229
O	0.00000000	3.47072507	2.80034851
O	0.00000000	2.39951071	4.66392252
O	0.00000000	−2.39951071	4.66392252
O	0.00000000	−3.47072507	2.80034851

Table S14. Cartesian coordinates (in Å) of (NO₂)₂BAI-PrmF at the M06-2X/aug-cc-pVTZ level of theory.

	<i>x</i>	<i>y</i>	<i>z</i>
C	1.12779469	−0.47737187	−0.00202675
I	−0.84537787	−0.86433232	−0.01433518
C	−4.27228615	−2.54160688	−0.05592536
N	−5.57380404	−2.78991370	−0.06390254
C	−6.38173291	−1.73696630	−0.04457950
C	−4.52174952	−0.29061130	−0.01122880
N	−3.70747415	−1.33628163	−0.03039097
H	−7.44677057	−1.93260253	−0.05095532
H	−3.60354104	−3.39346955	−0.07152362
H	−4.05552171	0.68866056	0.00953364
C	4.17871611	1.33582484	0.04144183
C	5.54021429	1.56359404	0.04914596
C	6.47633712	0.54897465	0.03088440
C	5.98059770	−0.73939341	0.00383246
C	4.63114909	−1.02987409	−0.00510543
C	3.71087533	0.02040237	0.01390974
H	3.49294165	2.16877719	0.05662343
H	7.53538999	0.75129221	0.03738293
H	4.30094950	−2.05696566	−0.02652222
C	2.30922412	−0.24821600	0.00529201
N	6.94562780	−1.86083041	−0.01651140
N	6.02291981	2.96184963	0.07837834
O	6.49193929	−2.98095957	−0.04008304
O	8.12054383	−1.57915216	−0.00815065
O	7.21875317	3.13392012	0.08458231
O	5.18760426	3.83564099	0.09403830
C	−6.79038765	0.72375140	0.00396960
C	−6.57447000	2.06524395	0.03144195
O	−8.12414572	0.47303120	−0.00412947
C	−7.86286777	2.67900717	0.04083167
H	−5.61948251	2.56095926	0.04359966
C	−8.75835134	1.66649890	0.01841758
H	−8.08731243	3.73047936	0.06146235
H	−9.83254798	1.62992923	0.01522001
C	−5.90631244	−0.42656679	−0.01713700

Table S15. Cartesian coordinates (in Å) of (NO₂)₂BAI-PrmT at the M06-2X/aug-cc-pVTZ level of theory.

	<i>x</i>	<i>y</i>	<i>z</i>
C	1.11598850	−0.52864538	0.00743656
I	−0.85134705	−0.94314810	0.00735479
C	−4.25940270	−2.66151884	0.03784008
N	−5.55853169	−2.92499662	0.02944184
C	−6.37490974	−1.88025806	0.00033238
C	−4.53686543	−0.41428674	−0.03867731
N	−3.70978313	−1.45066844	0.00673819
H	−7.43869962	−2.09427070	0.01244481
H	−3.58153729	−3.50569704	0.06976227
H	−4.08373119	0.56977165	−0.09305119
C	4.12934024	1.34219104	−0.01984934
C	5.48564615	1.59887020	−0.02022451
C	6.44296257	0.60439174	0.00416273

C	5.97459754	−0.69415505	0.02969347
C	4.63155803	−1.01336765	0.03141628
C	3.68939085	0.01712837	0.00630047
H	3.42615167	2.16041400	−0.03971087
H	7.49748811	0.82918643	0.00327274
H	4.32328220	−2.04727355	0.05188459
C	2.29342219	−0.27967832	0.00712359
N	6.96318275	−1.79472063	0.05644101
N	5.93869533	3.00702432	−0.04797364
O	6.53343325	−2.92428609	0.07857075
O	8.13183911	−1.48801015	0.05433886
O	7.13063324	3.20445907	−0.04738972
O	5.08510292	3.86284443	−0.06924295
C	−6.81663830	0.59073892	−0.06042011
C	−6.56751668	1.85650643	0.39094248
S	−8.40932118	0.48039180	−0.71856496
C	−7.66364386	2.73736722	0.20788492
H	−5.63892847	2.14221502	0.86302623
C	−8.72807485	2.12793744	−0.37963749
H	−7.66180411	3.77460368	0.50517170
H	−9.68326983	2.55383237	−0.63584513
C	−5.92126757	−0.56216990	−0.03351262

Table S16. Harmonic vibrational frequencies (in cm^{-1}), IR intensities (in km mol^{-1}), Raman activities (in $\text{\AA}^4 \text{amu}^{-1}$), and reduced masses (in \AA) of **PrmF** at the M06-2X/aug-cc-pVTZ level of theory.

Frequencies	IR Intensities	Raman Activities
29	0.3	0.0
112	0.1	0.1
152	0.1	0.2
257	0.8	3.1
362	0.1	3.6
413	0.1	0.4
440	3.8	2.5
488	4.8	0.4
616	8.2	0.3
643	10.7	2.6
707	0.4	1.1
749	13.9	0.1
756	0.3	4.5
779	82.2	2.3
848	8.0	1.0
906	5.5	6.7
915	0.4	2.1
936	15.4	13.9
958	4.8	2.8
1011	0.0	0.1
1035	0.4	0.0
1039	26.2	34.7
1052	12.2	5.3
1091	1.4	76.8
1132	8.0	23.3
1173	2.1	17.7
1202	2.3	22.0
1218	9.6	10.5
1232	15.3	2.9
1274	7.9	3.2
1336	6.0	43.7
1379	3.3	1.3
1428	3.1	50.5
1464	54.1	115.3
1495	34.6	12.3
1558	25.6	516.0
1629	53.5	3.3
1652	28.1	5.4

1680	2.3	845.4
3178	11.9	47.7
3200	11.3	62.2
3203	2.3	135.7
3280	3.1	76.3
3290	0.7	50.0
3309	0.5	173.3

Table S17. Harmonic vibrational frequencies (in cm^{-1}), IR intensities (in km mol^{-1}), Raman activities (in $\text{\AA}^4 \text{amu}^{-1}$), and reduced masses (in \AA) of **PrmT** at the M06-2X/aug-cc-pVTZ level of theory.

Frequencies	IR Intensities	Raman Activities
44	0.2	3.4
104	0.0	0.8
132	0.2	1
254	0.1	2.4
322	0.5	3.7
372	0.9	1.5
418	0.0	0.7
463	1.2	0.6
545	4.7	0.8
612	4.1	1.4
643	8.3	2.8
645	0.8	8.6
730	66.8	0.6
752	28.1	1.4
757	3.1	14.2
772	0.5	3.4
869	11.4	3.2
876	17.7	5.8
945	0.6	0.6
958	4.0	2.3
989	12.5	1.3
1014	0.6	4
1036	0.4	0.1
1067	5.6	17.1
1078	2.0	31.8
1103	1.8	25.3
1171	1.5	46.4
1200	0.9	13.8
1227	20.0	1
1261	8.5	1
1310	8.8	37.7
1377	5.2	19.1
1398	0.7	29.1
1465	51.3	148.3
1478	16.4	11.7
1509	46.6	358.6
1605	10.7	78.5
1628	59.4	2.7
1662	13.9	461.5
3170	11.4	41.7
3181	10.2	44.5
3202	9.9	156.7
3231	3.0	58.8
3246	1.3	137.8
3279	1.9	183

Table S18. Harmonic vibrational frequencies (in cm^{-1}), IR intensities (in km mol^{-1}), Raman activities (in $\text{\AA}^4 \text{amu}^{-1}$), and reduced masses (in \AA) of **(NO₂)₂BAI** at the M06-2X/aug-cc-pVTZ level of theory.

Frequencies	IR Intensities	Raman Activities
37	0.0	1.8
41	0.1	2.2
48	0.0	0.6

60	0.8	0.2
143	2.6	0.1
148	9.4	0.5
198	0.0	1.4
216	3.3	0.8
221	0.3	1.9
233	0.6	0.1
324	0.0	3.1
361	0.5	6.3
402	2.7	0.0
405	0.0	5.1
483	0.0	0.0
520	2.4	0.1
525	4.0	2.8
584	1.2	3.1
621	6.7	11.1
631	0.6	2.3
683	11.8	1.2
765	53.2	0.1
784	35.3	1.2
815	0.0	1.0
851	46.0	6.8
960	8.3	0.2
962	27.2	4.3
973	13.1	0.1
979	0.0	0.0
993	1.7	4.3
1022	0.4	76.7
1101	61.6	0.0
1144	14.9	18.9
1254	1.9	0.0
1292	10.6	186.7
1334	12.6	2.8
1457	332.0	17.6
1466	159.0	163.4
1473	20.8	23.0
1511	10.6	50.8
1643	21.0	22.8
1666	364.7	283.0
1698	138.2	1.3
1723	174.1	65.8
2331	73.7	2542.0
3254	0.2	57.7
3254	22.4	12.8
3266	44.1	35.6

Table S19. Harmonic vibrational frequencies (in cm^{-1}), IR intensities (in km mol^{-1}), Raman activities (in $\text{\AA}^4 \text{amu}^{-1}$), and reduced masses (in \AA) of $(\text{NO}_2)_2\text{BAI-PrmF}$ at the M06-2X/aug-cc-pVTZ level of theory.

Frequencies	IR Intensities	Raman Activities
5	0.1	0.3
7	0.3	1.5
13	0.4	1.4
27	0.1	3.1
28	0.1	1.8
42	0.1	3.7
48	0.0	0.5
54	0.3	0.2
58	2.1	4.6
71	4.1	5.8
81	1.0	2.2
115	0.7	0.1
142	8.9	3.6
155	7.5	0.1

158	0.1	0.1
199	0.0	1.3
215	1.8	11.0
239	2.5	0.5
249	1.1	0.7
258	0.8	3.0
332	0.0	3.5
361	0.2	5.5
364	0.3	5.1
405	2.3	0.0
414	0.1	1.9
422	0.3	3.4
442	2.5	5.2
484	0.0	0.0
493	3.7	0.5
522	2.3	0.1
523	1.0	0.7
588	0.9	3.9
608	0.1	0.7
615	8.0	0.4
632	0.5	2.7
650	25.3	8.6
686	11.0	1.7
705	0.4	1.0
746	14.1	0.1
759	1.7	9.3
764	52.5	0.2
783	73.1	2.5
784	40.3	1.4
816	0.0	1.0
849	73.2	4.2
853	6.3	0.9
906	6.1	7.9
919	0.3	2.5
938	14.4	23.1
958	5.3	3.0
962	27.1	4.5
962	2.3	0.1
971	19.2	0.3
984	0.1	0.0
989	10.4	18.1
1012	0.0	0.1
1022	0.4	99.6
1034	0.4	0.1
1040	27.3	47.7
1056	16.9	14.2
1091	9.5	149.1
1105	60.0	0.0
1132	21.1	36.2
1146	11.2	38.5
1173	1.8	25.2
1205	1.7	16.0
1221	20.0	24.1
1232	38.4	5.7
1257	2.1	0.1
1275	7.6	1.9
1290	30.3	329.5
1335	13.0	3.5
1339	5.1	42.1
1379	2.5	2.2
1429	3.5	72.3
1457	326.6	22.0
1465	63.2	166.3
1466	168.5	233.6
1472	23.5	30.0

1498	41.4	27.0
1510	23.0	93.1
1557	38.6	689.0
1630	68.8	22.2
1642	21.6	22.4
1657	74.3	9.6
1664	421.1	446.0
1681	0.9	1049.8
1696	134.8	1.6
1721	148.2	131.1
2321	117.2	3912.9
3181	7.5	22.9
3202	5.0	58.9
3205	0.8	98.9
3252	9.7	31.0
3255	10.5	32.1
3267	49.0	34.7
3280	2.9	73.0
3290	1.1	56.9
3310	0.8	202.7

Table S20. Harmonic vibrational frequencies (in cm^{-1}), IR intensities (in km mol^{-1}), and Raman activities (in $\text{\AA}^4 \text{amu}^{-1}$), and reduced masses (in \AA) of $(\text{NO}_2)_2\text{BAI-PrmT}$ at the M06-2X/aug-cc-pVTZ level of theory.

Frequencies	IR Intensities	Raman Activities
3	0.2	0.5
5	0.2	1.5
8	0.2	1.8
27	0.0	1.8
29	0.1	4.6
44	0.0	2.9
48	0.0	0.6
57	1.4	2.6
57	1.1	3.6
70	3.4	5
81	1.2	2.4
108	0.5	1.5
140	0.3	1
142	9.5	3.8
155	7.5	0.2
199	0.0	1.3
215	1.8	11.1
238	2.4	0.5
248	0.9	0.8
254	0.2	2.2
324	0.1	7.1
333	0.0	2.7
361	0.2	5.9
374	0.4	2.6
404	2.4	0
414	0.0	3.7
425	0.2	2
465	0.8	1.5
484	0.0	0
522	2.3	0.1
523	1.0	0.7
546	4.2	1.1
587	0.9	3.9
608	0.1	0.7
611	4.8	1.5
632	0.4	2.7
645	4.7	7.8
651	18.7	10.1
686	10.9	1.7

735	62.2	0.6
750	29.9	0.8
760	0.8	22.7
764	52.5	0.2
772	0.7	4.8
784	35.7	1.5
816	0.0	0.9
849	74.4	4.5
874	10.6	4.5
878	23.7	3.1
949	0.6	0.6
961	4.3	2.8
961	3.0	0.1
962	27.0	4.4
971	18.5	0.3
983	0.0	0
989	14.6	20.1
996	21.0	4.3
1016	0.6	4.8
1022	0.4	101.2
1035	0.4	0
1068	7.2	38.7
1079	4.3	59.2
1106	2.9	36.7
1107	59.5	0
1144	11.0	39.9
1172	4.1	74.8
1206	1.1	16.9
1226	55.1	1.9
1256	1.9	0.1
1262	10.4	0.7
1290	30.4	331.1
1312	10.3	47.8
1334	13.1	3.6
1377	4.5	29.9
1399	1.4	38.5
1457	325.5	21.7
1466	53.0	201.1
1466	173.3	257.6
1472	24.3	29.9
1479	16.0	20.4
1508	73.7	452.3
1510	21.8	91.8
1605	12.4	88.1
1634	108.0	42.6
1642	22.0	22.2
1663	28.5	546.4
1664	412.5	475.2
1696	134.4	1.4
1721	150.0	130.7
2320	117.5	3950.8
3174	11.8	66.4
3182	6.4	20.7
3203	2.2	87.6
3231	2.7	57.8
3248	1.2	121.2
3253	9.6	30.8
3255	10.5	32.2
3268	49.4	34.8
3279	2.8	223.3

Table S21. Point group symmetries, binding energies (E_{bind} in kcal mol⁻¹), halogen bond intermolecular separation ($R_{\text{I} \cdots \text{N}}$ in Å), halogen bond angle ($\alpha_{\text{C-I} \cdots \text{N}}$ in °), and percent reduction in the

sum of van der Waals radii upon complexation (%rsvdW) of the halogen bond complexes at the M06-2X/aug-cc-pVTZ level of theory.

Complex	Symmetry	E_{bind}^a	$R_{\text{I}\cdots\text{N}}$	$\alpha_{\text{C-I}\cdots\text{N}}$	%rsvdW ^b
(NO ₂) ₂ BAI-PrmF	C _s	−6.99	2.90	178	30.5
(NO ₂) ₂ BAI-PrmT	C ₁	−6.92	2.90	178	30.5

$$^a E_{\text{bind}} = E_{\text{complex}} - E_{\text{acceptor}} - E_{\text{donor}}$$

^b Relative to the sum of nitrogen (1.79 Å) and iodine (2.38 Å) van der Waals radii.¹

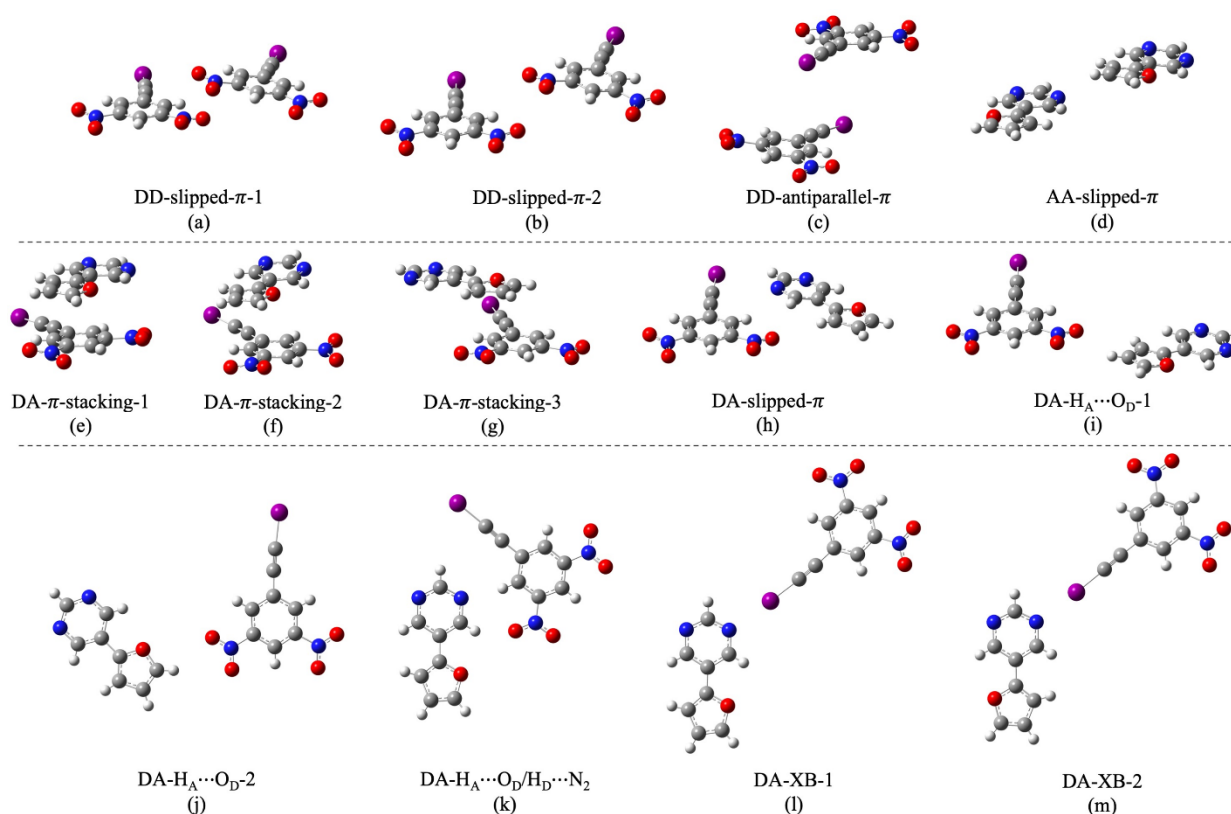


Figure S3. Energetically competitive pairwise contacts in the experimental crystal structure of (NO₂)₂BAI-PrmF. DD, AA, and DA denote a donor-donor, acceptor-acceptor, and a donor-acceptor interaction.

Table S22. Interaction energies, with ($E_{\text{int}}^{\text{CP}}$ in kcal mol^{−1}) and without (E_{int} in kcal mol^{−1}) the Boys-Bernardi counterpoise (CP) procedure,² and the average of the two ($E_{\text{int}}^{\text{Avg}}$ in kcal mol^{−1}; kJ mol^{−1} in parenthesis) observed in the experimental crystal structure of (NO₂)₂BAI-PrmF.

Contact	E_{int}	$E_{\text{int}}^{\text{CP}}$	$E_{\text{int}}^{\text{Avg}}$
(a) DD-slipped- π -1	−1.6	−1.4	−1.5 (−6.3)
(b) DD-slipped- π -2	−1.5	−1.3	−1.4 (−5.6)
(c) DD-antiparallel- π	−0.9	−0.8	−0.9 (−3.8)
(d) AA-slipped- π	−0.9	−0.8	−0.9 (−3.8)
(e) DA- π -stacking-1	−7.7	−6.9	−7.3 (−30.5)
(f) DA- π -stacking-2	−7.8	−7.1	−7.4 (−31.0)
(g) DA- π -stacking-3	−6.4	−5.9	−6.2 (−25.9)
(h) DA-slipped- π	−3.8	−3.6	−3.7 (−15.5)
(i) DA-H _A ...O _D -1	−1.1	−1.0	−1.1 (−4.6)
(j) DA-H _A ...O _D -2	−1.6	−1.5	−1.5 (−6.3)
(k) DA-H _A ...O _D /H _D ...N _A	−4.2	−3.8	−4.0 (−16.7)
(l) DA-XB-1	−7.2	−7.1	−7.1 (−29.7)
(m) DA-XB-2	−7.0	−6.9	−7.0 (−29.3)

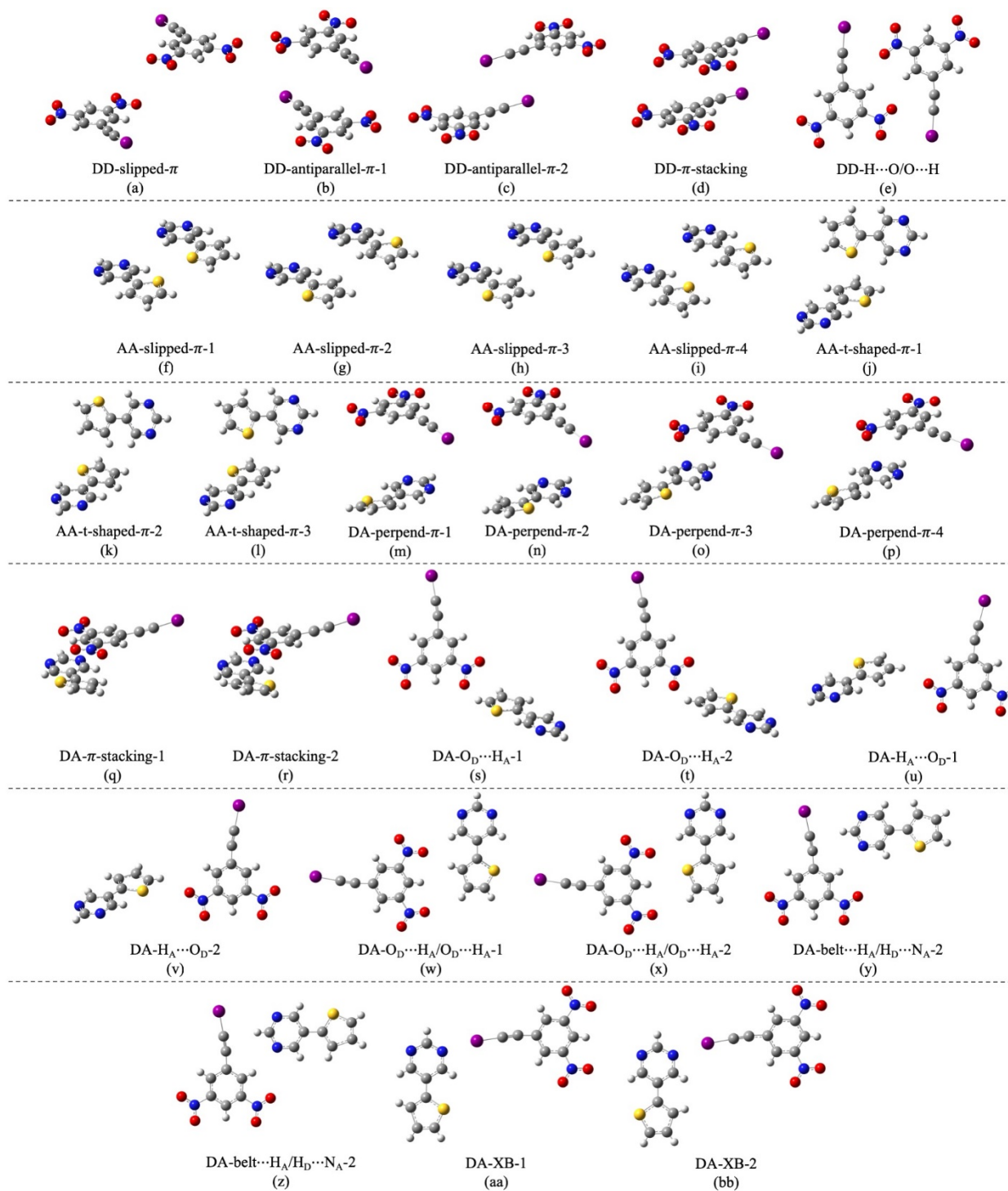


Figure S4. Energetically competitive pairwise contacts in the experimental crystal structure of $(\text{NO}_2)_2\text{BAI-PrmT}$. DD, AA, and DA denote a donor-donor, acceptor-acceptor, and a donor-acceptor interaction.

Table S23. Interaction energies, with ($E_{\text{int}}^{\text{CP}}$ in kcal mol $^{-1}$) and without (E_{int} in kcal mol $^{-1}$) the Boys-Bernardi counterpoise (CP) procedure,² and the average of the two ($E_{\text{int}}^{\text{Avg}}$ in kcal mol $^{-1}$; kJ mol $^{-1}$ in parenthesis) observed in the experimental crystal structure of $(\text{NO}_2)_2\text{BAI-PrmT}$.

Contact	E_{int}	$E_{\text{int}}^{\text{CP}}$	$E_{\text{int}}^{\text{Avg}}$
(a) DD-slipped- π	−0.8	−0.8	−0.8 (−3.3)
(b) DD-antiparallel- π -1	−1.6	−1.5	−1.6 (−6.7)
(c) DD-antiparallel- π -2	−0.8	−0.7	−0.7 (−2.9)
(d) DD- π -stacking	−5.5	−5.0	−5.2 (−21.8)

(e) DD-H \cdots O/O \cdots H	-4.2	-3.9	-4.0 (-16.7)
(f) AA-slipped- π -1	-1.7	-1.4	-1.5 (-6.3)
(g) AA-slipped- π -2	-1.9	-1.6	-1.8 (-7.5)
(h) AA-slipped- π -3	-2.0	-1.7	-3.7 (-15.5)
(i) AA-slipped- π -4	-1.5	-1.2	-1.3 (-5.4)
(j) AA-t-shaped- π -1	-3.3	-2.9	-3.1 (-13.0)
(k) AA-t-shaped- π -2	-3.0	-2.7	-2.8 (-11.7)
(l) AA-t-shaped- π -3	-3.2	-2.8	-3.0 (-12.6)
(m) DA-perpend- π -1	-1.2	-1.1	-1.2 (-5.0)
(n) DA-perpend- π -2	-1.3	-1.2	-1.2 (-5.0)
(o) DA-perpend- π -3	-4.1	-3.7	-3.9 (-16.3)
(p) DA-perpend- π -4	-4.0	-3.6	-3.8 (-15.9)
(q) DA- π -stacking-1	-7.4	-6.7	-7.0 (-29.3)
(r) DA- π -stacking-2	-7.6	-6.9	-7.2 (-30.1)
(s) DA-OD \cdots HA-1	-2.2	-2.1	-2.2 (-9.2)
(t) DA-OD \cdots HA-2	-2.1	-2.0	-2.0 (-8.4)
(u) DA-HA \cdots OD-1	-1.2	-1.1	-1.1 (-4.6)
(v) DA-HA \cdots OD-2	-0.7	-0.6	-0.6 (-2.5)
(w) DA-OD \cdots HA/OD \cdots HA-1	-2.1	-1.8	-2.0 (-8.4)
(x) DA-OD \cdots HA/OD \cdots HA-2	-1.6	-1.3	-1.5 (-6.3)
(y) DA-belt \cdots HA/ HD \cdots NA-1	-3.1	-2.9	-3.0 (-12.6)
(z) DA-belt \cdots HA/ HD \cdots NA-1	-3.2	-3.0	-3.1 (-13.0)
(aa) DA-XB-1	-6.8	-6.7	-6.8 (-28.5)
(bb) DA-XB-2	-6.8	-6.7	-6.8 (-28.5)

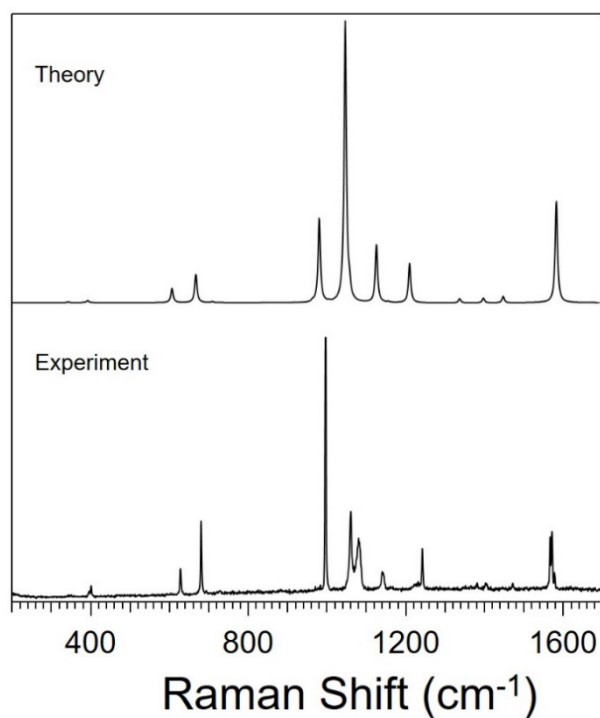


Figure S5. Experimental Raman spectra of **Prm** compared to its simulated spectrum (top).

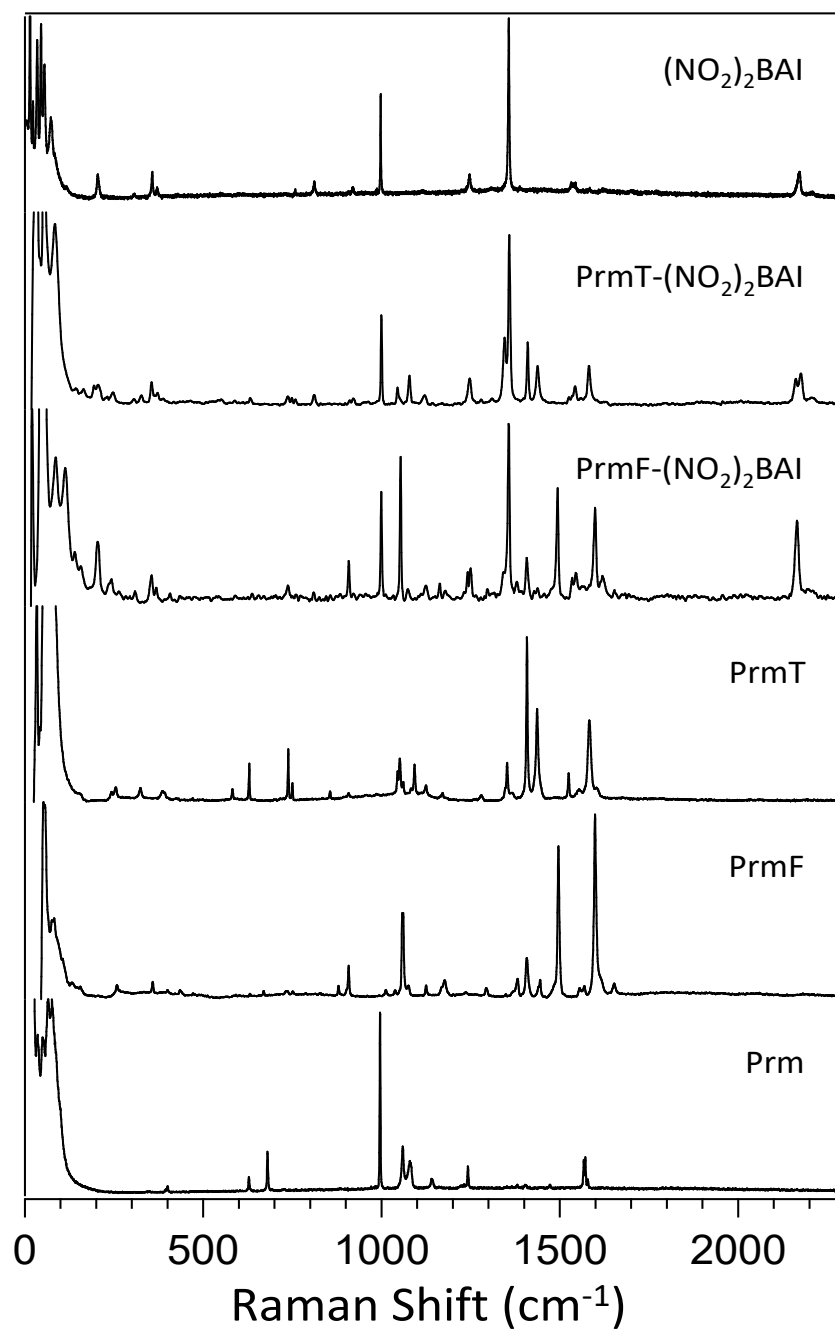


Figure S6. Experimental Raman spectra of **Prm**, **PrmF**, **PrmT**, **PrmF- $(\text{NO}_2)_2\text{BAI}$** , **PrmT- $(\text{NO}_2)_2\text{BAI}$** , and **$(\text{NO}_2)_2\text{BAI}$** .

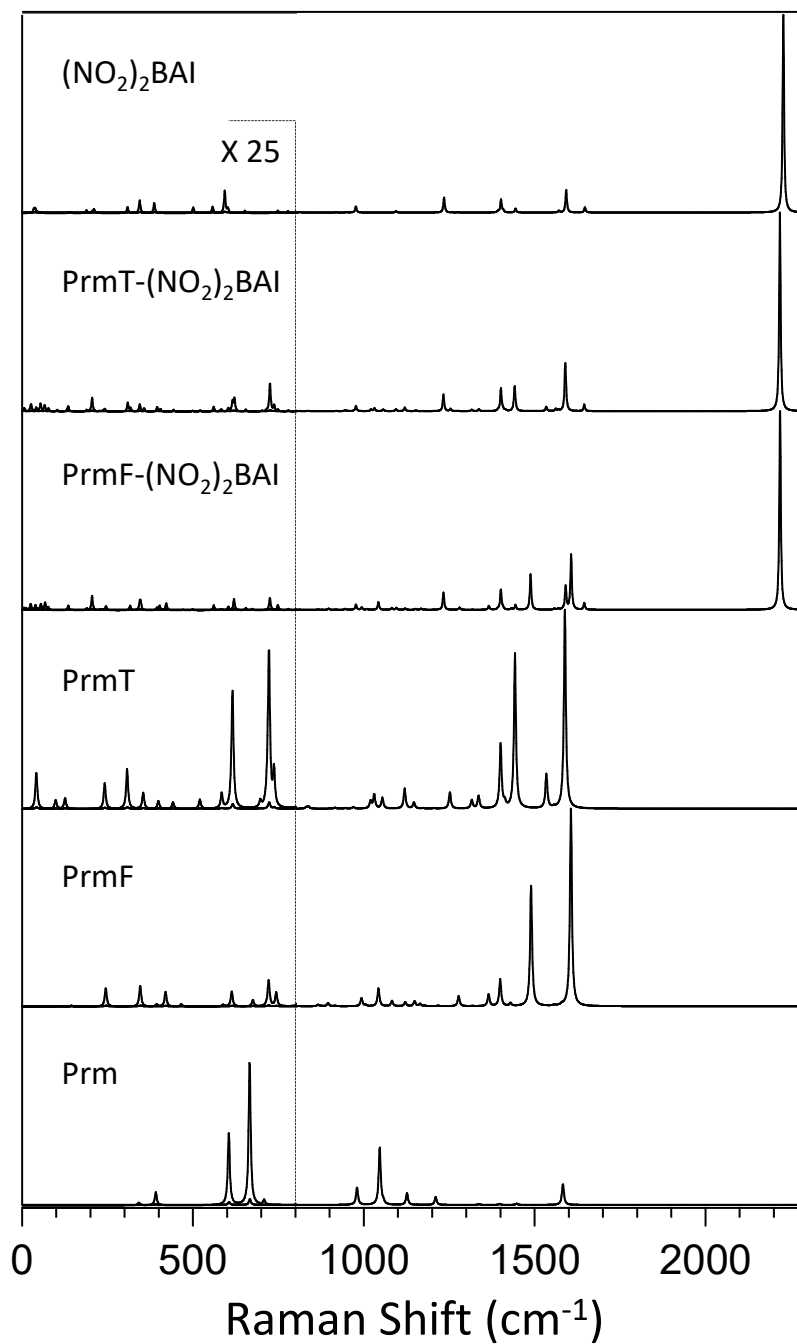


Figure S7. Simulated Raman spectra of Prm, PrmF, PrmT, PrmF-(NO₂)₂BAI, PrmT-(NO₂)₂BAI, and (NO₂)₂BAI.

References

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