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Supporting Information

Topochemical, Single-Crystal-to-Single-Crystal [2+2] Photocycloadditions Driven by Chalcogen-Bonding Interactions

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Electronic Supplementary Information

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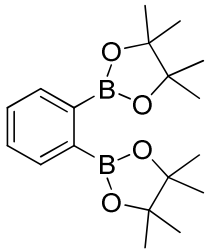
I) General considerations

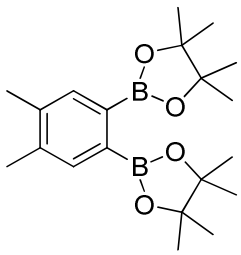
Oxygen- and moisture-sensitive experiments were carried out under a dry oxygen-free argon atmosphere using standard Schlenk techniques. Solvents were dried by standard methods. The NMR spectra were recorded on Bruker spectrometers (300 MHz) referenced to residual solvent signals as internal standards. Elemental analyses were performed at Centre Regional de Mesures Physiques de l'Ouest (CRMPO) with Elementar Vario/Perkin Elmer 2400 series. Single crystal XRD were performed at Centre de Diffraction de Rennes (CDIFX) with a Bruker AXS D8 Venture diffractometer. (*E*)-1,2-di(4-pyridyl)ethylene (**bpen**) was obtained from Aldrich and used as received.

II) General procedure for the Miyaura borylation reactions

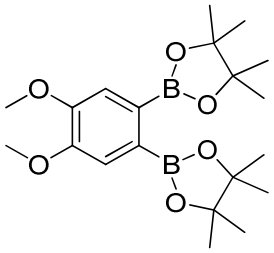
To bis(pinacolato)diborane (2.5 mmol), anhydrous potassium acetate (6 mmol) and a dibromo derivative (1 mmol) 3.5 ml of anhydrous DMF was added and the mixture was degassed with argon. [1,1'-Bis(diphenylphosphino)ferrocene]palladium(II) dichloride (73 mg, 0.1 mmol) was added and the mixture was stirred in argon atmosphere at 80°C overnight. After cooling to room temperature, the mixture was poured to a separatory funnel, diluted with water and extracted with AcOEt (50 ml). The aqueous layer was discarded and the organic layer was washed with water (twice) and brine and then dried over $MgSO_4$. Volatiles were removed on a rotavap and the crude product was purified by flash chromatography (petroleum ether:AcOEt = 9:1) to give pure diboronic acid pinacol diesters **4**–**6**.



4: Yield: 52%. White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.73–7.61 (m, 2H), 7.44–7.35 (m, 2H), 1.39 (s, 24H). ^{11}B NMR (96 MHz, $CDCl_3$): δ 31.57. ^{13}C NMR (75 MHz, $CDCl_3$): δ 133.46, 129.12, 83.84, 24.90.



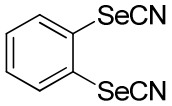
5: Yield: 61%. White solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45 (s, 2H), 2.27 (s, 6H), 1.38 (s, 24H). ^{11}B NMR (96 MHz, $CDCl_3$): δ 31.50. ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.57, 135.02, 83.62, 24.89, 19.56.



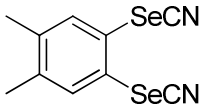
6: Yield: 50%. Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.17 (s, 2H), 3.92 (s, 6H), 1.38 (s, 24H). ^{11}B NMR (96 MHz, $CDCl_3$): δ 31.26. ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.74, 116.29, 83.74, 55.74, 24.89.

III) General procedure for the synthesis of the bis(selenocyanato)arenes

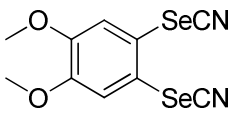
To SeO_2 (6 mmol) and malononitrile (2 mmol) 2 ml of anhydrous DMSO was added in argon atmosphere and the mixture was stirred for 30 min at room temperature. To the resulting orange solution diboronic acid pinacol diester **4**–**6** (1 mmol) was added and the mixture was stirred at 60°C overnight. After cooling to room temperature water (10 ml) was added and the mixture was extracted with DCM (3x 20 ml). The organic layers were combined, dried with $MgSO_4$ and volatiles were removed on a rotavap. The crude product was purified by column chromatography (petroleum ether:DCM = 1:1 or petroleum ether:AcOEt = 9:1) to give pure bis(selenocyanato)arenes **1**–**3**.



1: Yield: 74%. Dark yellow solid, mp 111–113°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.98–7.86 (m, 2H), 7.61–7.50 (m, 2H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 135.26, 131.76, 130.22, 105.55. ^{77}Se NMR (76 MHz, DMSO-d_6): δ 337.34. Elem. Anal. calcd for $C_8H_4N_2Se_2$: C, 33.59; H, 1.41; N, 9.79 found: C, 33.80; H, 1.37; N, 9.57.

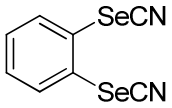


2: Yield: 90%. Pale yellow needles, mp 112–113°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.68 (s, 2H), 2.28 (s, 6H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 141.07, 135.92, 126.74, 105.80, 19.37. ^{77}Se NMR (76 MHz, DMSO-d_6): δ 329.51. Elem. Anal. calcd for $C_{10}H_8N_2Se_2$: C, 38.24; H, 2.57; N, 8.92 found: C, 38.40; H, 2.63; N, 8.87.

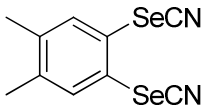


3: Yield: 88%. Dark yellow columns, mp 122–123°C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.42 (s, 2H), 3.84 (s, 6H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 151.09, 120.84, 118.04, 105.83, 56.59. ^{77}Se NMR (76 MHz, DMSO-d_6): δ 341.92. Elem. Anal. calcd for $C_{10}H_8N_2O_2Se_2$: C, 34.70; H, 2.33; N, 8.09 found: C, 34.98; H, 2.24; N, 7.73.

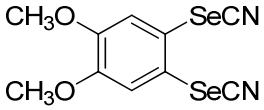
IV) Crystallizations



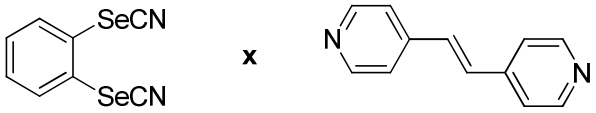
1: The compound was dissolved in small amount of $CHCl_3$ and left for slow evaporation of the solvent. After one day yellow rods appeared (mp 111–113°C).



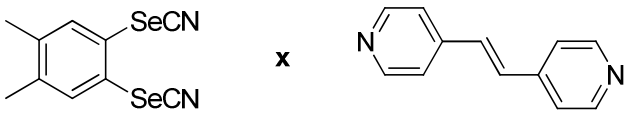
2: The compound was dissolved in small amount of hot AcOEt and petroleum ether was added in portions. Resulting solution was left to cool down yielding white needles (mp 112–113°C).



3: The compound was dissolved in small amount of hot AcOEt and petroleum ether was added in portions. Resulting solution was left to cool down yielding dark yellow rods (mp 122–123°C).



$(1)_4(bpen)_5$: In a test tube, 7 mg (0.025 mmol) of **1** and 4.5 mg (0.025 mmol) of (*E*)-1,2-di(4-pyridyl)ethylene were dissolved in 1 ml of AcOEt and left for slow evaporation of the solvent. After two days light brown plates appeared (mp 123–125°C).
Larger scale crystallization was performed in different way. In a test tube 57 mg (0.2 mmol) of *o*-Se_2 and 54.6 mg (0.3 mmol) (*E*)-1,2-di(4-pyridyl)ethylene were dissolved in minimum amount of hot AcOEt and left to cool to room temperature and then refrigerated overnight. Light brown rods were obtained having the same crystal structure.
Elem. Anal. Calcd for $(C_8H_4N_2Se_2)_4 \cdot (C_{12}H_{10}N_2)_5$: C, 53.76; H, 3.24; N, 12.27. Found: C, 54.18; H, 3.24; N, 11.94.



$(2)_2(bpen)_3 \cdot H_2O$: In a test tube, 8 mg (0.025 mmol) of **2** and 7 mg (0.038 mmol) of (*E*)-1,2-di(4-pyridyl)ethylene were dissolved in 1 ml of AcOEt and cooled in a freezer. After two days light yellow blocks appeared (mp 109–111°C).
Elem. Anal. Calcd for $(C_{10}H_8N_2Se_2)_2 \cdot (C_{12}H_{10}N_2)_3 \cdot (H_2O)$: C, 56.38; H, 4.06; N, 11.74. Found: C, 56.63; H, 3.93; N, 11.77

(3)(bpen)$_2$: In a test tube, 17 mg (0.05 mmol) of **3** and 14 mg (0.075 mmol) of (*E*)-1,2-di(4-pyridyl)ethylene were dissolved in 1 ml of AcOEt. On top of the solution pentane was added slowly to prevent mixing of the solvents and the test tube was sealed. After one day, light brown blocks of (**3**)(**bpen**)$_2$ co-crystal appeared (mp 142–144°C), together with a few dark yellow plates of starting **3**. Due to the very similar colour and shape of the two phases, the manual separation of the crystals was not possible and elemental analysis was not performed.

V) Photo reactions of (1)$_4$(bpen)$_5$ and (3)(bpen)$_2$

Crystals of **(1)$_4$(bpen)$_5$** were placed in a drop of Paraton® oil on a glass plate and exposed to 254 nm UV radiation under a 6W laboratory lamp for two hours. A small piece of the resulting crystals was cut and used for single crystal X-ray diffraction experiment.

Crystals of **(3)(bpen)$_2$** were placed in a drop of Paraton® oil on a glass plate and exposed for 4 days to 253.7 nm (35W) UV radiation in a Rayonet RPR-100 reactor. A small piece of the resulting crystals was cut and used for single crystal X-ray diffraction experiment.

VI) Crystallographic data

Table S1. Crystallographic data

Compound	**1**	**$(1)_4(bpen)_5$**	**$(1)_4(bpen)_5$_UV**
CCDC	2168861	2168862	2168863
Formula	$C_{16}H_8N_4Se_4$	$C_{46}H_{33}N_9Se_4$	$C_{46}H_{33}N_9Se_4$
FW ($g \cdot mol^{-1}$)	572.10	1027.65	1027.65
T (K)	150(2)	150(2)	150(2)
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$
a (Å)	8.4085(16)	11.6753(15)	11.728(3)
b (Å)	8.6435(16)	13.4635(18)	13.493(3)
c (Å)	12.302(2)	14.1333(19)	14.181(4)
α (deg)	90	97.259(5)	102.197(8)
β (deg)	91.617(7)	106.066(5)	103.967(9)
γ (deg)	90	100.621(5)	99.515(8)
V ($Å^3$)	893.7(3)	2060.9(5)	2072.5(9)
Z	2	2	2
Cryst. dim. (mm)	0.15 × 0.04 × 0.03	0.16 × 0.13 × 0.11	0.12 × 0.05 × 0.04
Dcalc ($g \cdot cm^{-1}$)	2.126	1.656	1.647
Radiation source	Mo-Kα	Mo-Kα	Mo-Kα
μ (mm^{-1})	8.214	3.607	3.587
Total refls	10125	23883	39151
Abs. corr.	multi-scan	multi-scan	multi-scan
Uniq refls (R_{int})	2447 (0.0432)	9320 (0.0402)	9372 (0.1537)
Data / restraints / parameters	2447 / 0 / 109	9320 / 1 / 531	9372 / 28 / 363
GOF	1.059	1.025	1.119
R1, wR2 ($I > 2\sigma(I)$)	0.0241, 0.0509	0.0326, 0.0801	0.1490, 0.3308
R1, wR2 (all data)	0.0337, 0.0539	0.0439, 0.0853	0.2186, 0.3854
Res. dens. ($e/Å^3$)	0.442, −0.476	1.011, −0.964	2.947, −1.669

Table S1. Crystallographic data (continued)

Compound	**2**	**(2)$_2$(bpen)$_3$**·H_2O
CCDC	2168864	2168865
Formula	$C_{10}H_8N_2Se_2$	$C_{28}H_{24}N_5O_{0.50}Se_2$
FW (g·mol^{-1})	314.10	596.44
T (K)	150(2)	150(2)
Crystal system	orthorhombic	triclinic
Space group	*Pna*2$_1$	$P\bar{1}$
a (Å)	16.244(2)	9.3060(11)
b (Å)	14.789(2)	11.5362(12)
c (Å)	4.5394(6)	12.4900(13)
α (deg)	90	99.615(4)
β (deg)	90	100.189(4)
γ (deg)	90	93.830(4)
V (Å^3)	1090.5(2)	1294.8(2)
Z	4	2
Cryst. dim. (mm)	0.13 × 0.04 × 0.03	0.16 × 0.11 × 0.08
Dcalc (g·cm^{-1})	1.913	1.530
Radiation source	Mo-Kα	Mo-Kα
μ (mm^{-1})	6.741	2.884
Total refls	4365	14148
Abs. corr.	multi-scan	multi-scan
Uniq refls (R_{int})	2305 (0.0338)	5767 (0.0298)
Data / restraints / parameters	2305 / 1 / 129	5767 / 0 / 330
GOF	0.953	1.016
R1, wR2 (I > 2σ(I))	0.0390, 0.0530	0.0240, 0.0553
R1, wR2 (all data)	0.0699, 0.0592	0.0315, 0.0587
Res. dens. (e/Å^3)	0.471, –0.502	0.316, –0.339

Table S1. Crystallographic data (continued)

Compound	**3**	**(3)(bpen)$_2$**	**(3)(bpen)$_2$_UV**
CCDC	2168866	2168867	2168868
Formula	$C_{20}H_{16}N_4O_4Se_4$	$C_{34}H_{28}N_6O_2Se_2$	$C_{34}H_{28}N_6O_2Se_2$
FW (g·mol^{-1})	692.21	710.54	710.54
T (K)	150(2)	150(2)	150(2)
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	17.0174(16)	8.3072(8)	8.178(3)
b (Å)	16.4008(14)	9.7665(12)	9.994(3)
c (Å)	8.2652(9)	19.299(2)	19.128(5)
α (deg)	90	99.209(4)	93.184(9)
β (deg)	95.415(4)	89.903(4)	98.073(10)
γ (deg)	90	101.303(4)	102.060(10)
V (Å^3)	2296.5(4)	1514.9(3)	1507.9(8)
Z	4	2	2
Cryst. dim. (mm)	0.18 × 0.06 × 0.01	0.16 × 0.08 × 0.06	0.11 × 0.08 × 0.02
Dcalc (g·cm^{-1})	2.002	1.558	1.565
Radiation source	Mo-Kα	Mo-Kα	Mo-Kα
μ (mm^{-1})	6.425	2.483	2.495
Total refls	35565	37808	30655
Abs. corr.	multi-scan	multi-scan	multi-scan
Uniq refls (R_{int})	5254 (0.0686)	6931 (0.0269)	6870 (0.0618)
Data / restraints / parameters	5254 / 0 / 293	6931 / 0 / 399	6870 / 24 / 388
GOF	1.089	1.030	1.090
R1, wR2 (I > 2σ(I))	0.0417, 0.1081	0.0216, 0.0531	0.0974, 0.2513
R1, wR2 (all data)	0.0495, 0.1145	0.0251, 0.0547	0.1139, 0.2609
Res. dens. (e/Å^3)	1.855, –1.163	0.385, –0.295	3.529, –4.093

VII) ESP calculations

The geometry of molecules **1**–**3** was optimized starting from their "*syn*" conformation using the Gaussian 16 program using the B3LYP method with D3 Grimme dispersion correction and the Def2TZVPP basis set (as reported in A. Dhaka, O. Jeannin, E. Aubert, E. Espinosa M. Fourmigué, *Chem. Commun*. **2021**, *57*, 4560). For compound **3**, preliminary optimizations with HF/6-311G were performed to shorten the time during the second calculation with more complex method and basis set. Frequency calculations were also performed in order to check that true energy minima were obtained.
ESP maps generated with isovalue = 0.002 are presented below. The values for both 0.001 and 0.002 isovalue are summarized in Table S1.

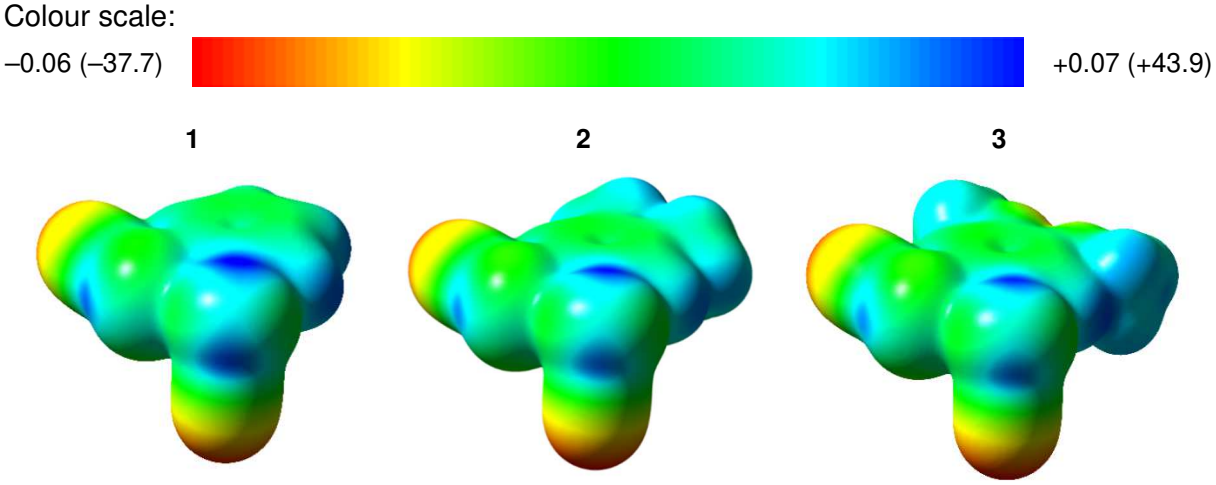


Figure S1. Electrostatic Potential (ESP) surface (plotted on the 0.002 e/bohr^3 isosurface of the electronic density) for compounds **1**–**3**. Colour range from –37.7 (red) to +43.9 (blue) kcal/mol.

Table S2: ESP values in kcal/mol for compounds **1**–**3**.

isovalue	Compound	**ESP on Se** opposite to CN	**ESP on Se** opposite to Ph	**ESP on N**	
0.001	**1**	+36.1 -	+28.0 +25.2	–34.4 –32.8	SeCN perp. SeCN in plane
	2	+33.1 -	+25.4 +22.8	–35.8 –33.9	SeCN perp. SeCN in plane
	3	+31.6 -	+24.5 +22.7	–36.1 –32.6	SeCN perp. SeCN in plane
0.002	**1**	+46.2 -	+37.6 +34.8	–38.6 –37.0	SeCN perp. SeCN in plane
	2	+43.0 -	+34.7 +32.3	–40.2 –38.2	SeCN perp. SeCN in plane
	3	+41.2 -	+33.9 +32.1	–40.5 –37.0	SeCN perp. SeCN in plane

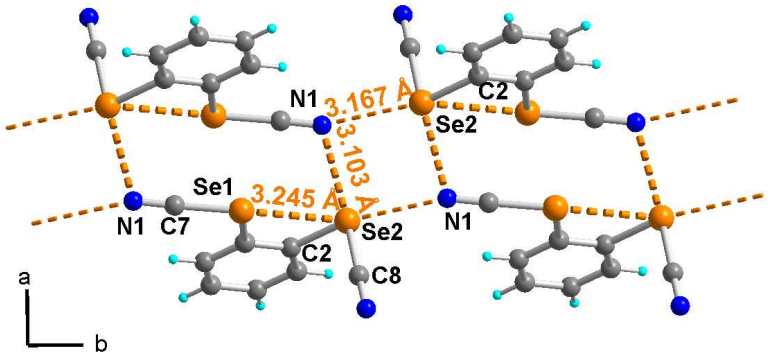


Figure S2 Network of ChB interactions in **1**. See Table S2 for structural characteristics. Hydrogen atoms were omitted for clarity.

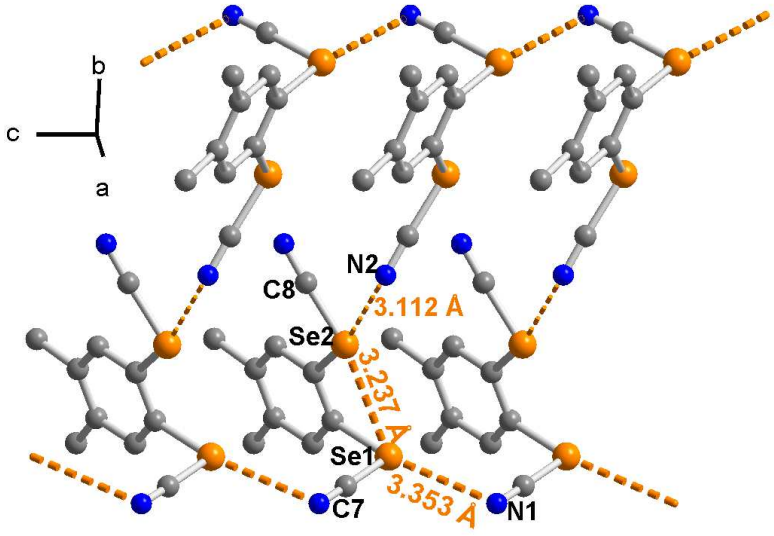


Figure S3 Network of ChB interactions in **2**. See Table S2 for structural characteristics. Hydrogen atoms were omitted for clarity.

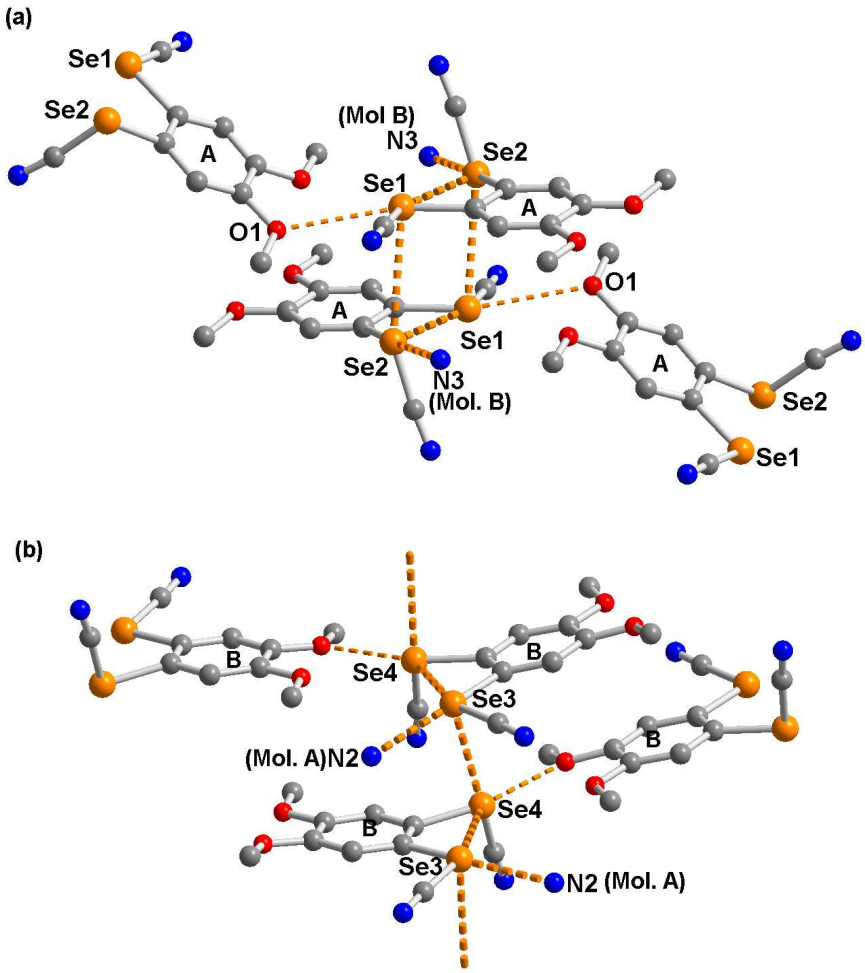


Figure S4 Network of ChB interactions for the two crystallographically independent molecules in **3** for (a) molecule A and (b) molecule B. See Table S2 for structural characteristics. Hydrogen atoms were omitted for clarity.

Table S3. Chalcogen bond characteristics in **1**–**3**. See Figures S2-S4 for atom numbering

Compound	ChB	ChB length (Å)	RR	ChB angle (°)
Compound **1**	N≡C–Se1···Se2[i]	3.245(1)	0.85	155.09(8)
	N≡C–Se2···N1[ii]	3.103(10)	0.90	174.41(9)
	C_{Ar}–Se2···N1[iii]	3.167(3)	0.92	168.77(6)
Compound **2**	N≡C–Se2···Se1[i]	3.237(1)	0.85	158.8(2)
	C_{Ar}–Se2···N2[iv]	3.112(7)	0.90	166.5(2)
	N≡C–Se1···η_6[v]	3.461	0.96	175.7
	C_{Ar}–Se1···N1[vi]	3.353(7)	0.97	171.7(2)
Compound **3**	N≡C–Se1···Se2[i]	3.216(6)	0.85	157.7(1)
	C_{Ar}–Se1···O1[vii]	3.312(3)	0.97	164.4(1)
	N≡C–Se2···Se1[viii]	3.499(6)	0.92	158.7(1)
	C_{Ar}–Se2···N3[ix]	3.163(5)	0.92	176.7(1)
	N≡C–Se3···Se4[i]	3.221(7)	0.85	158.5(1)
	C_{Ar}–Se3···N2[x]	3.334(6)	0.97	176.9(1)
	N≡C–Se4···Se3[xi]	3.409(6)	0.90	169.1(1)
	C_{Ar}–Se4···O4[xii]	3.077(4)	0.90	154.1(1)

[i] Intramolecular ChB. [ii] 2–*x*, 1–*y*, 1–*z*. [iii] *x*, 1+*y*, *z*. [iv] 1–*x*, 1–*y*, –0.5+*z*. [v] η_6 stands for the centroid of the benzene ring. [vi] *x*, *y*, –1+*z*. [vii] 1–*x*, –0.5+*y*, 0.5–*z*. viii 1–*x*, 1–*y*, 1–*z*. [ix] *x*, *y*, *z*. [x] *x*, 0.5–*y*, 0.5+*z*. [xi] *x*, 0.5–*y*, 0.5+*z*. [xii] 2–*x*, –0.5+*y*, 2.5–*z*.

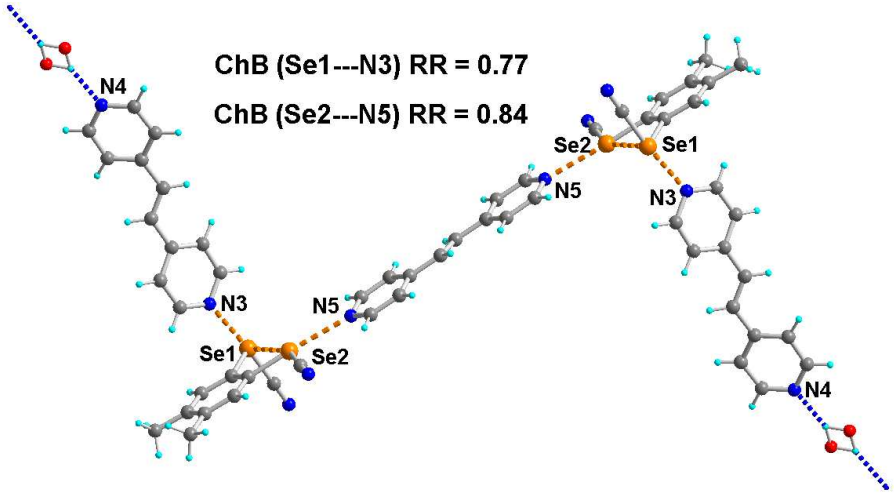


Figure S5. Detail of the intermolecular (HB as blue, ChB as orange dotted lines) interactions in **(2)$_2$(bpen)$_3$**·H_2O

Table S4 Chalcogen bond characteristics in **(2)$_2$(bpen)$_3$**·H_2O. See Figure S5 for atom numbering

ChB	ChB length (Å)	RR	ChB angle (°)
NC–Se1···N3$_{Py}$	2.645(3)	0.77	174.51(7)
NC–Se2···Se1^{i}	3.239(7)	0.85	157.64(6)
C_{Ar}–Se2···N5$_{Py}$	2.898(6)	0.84	170.98(6)

^{i} Intramolecular ChB

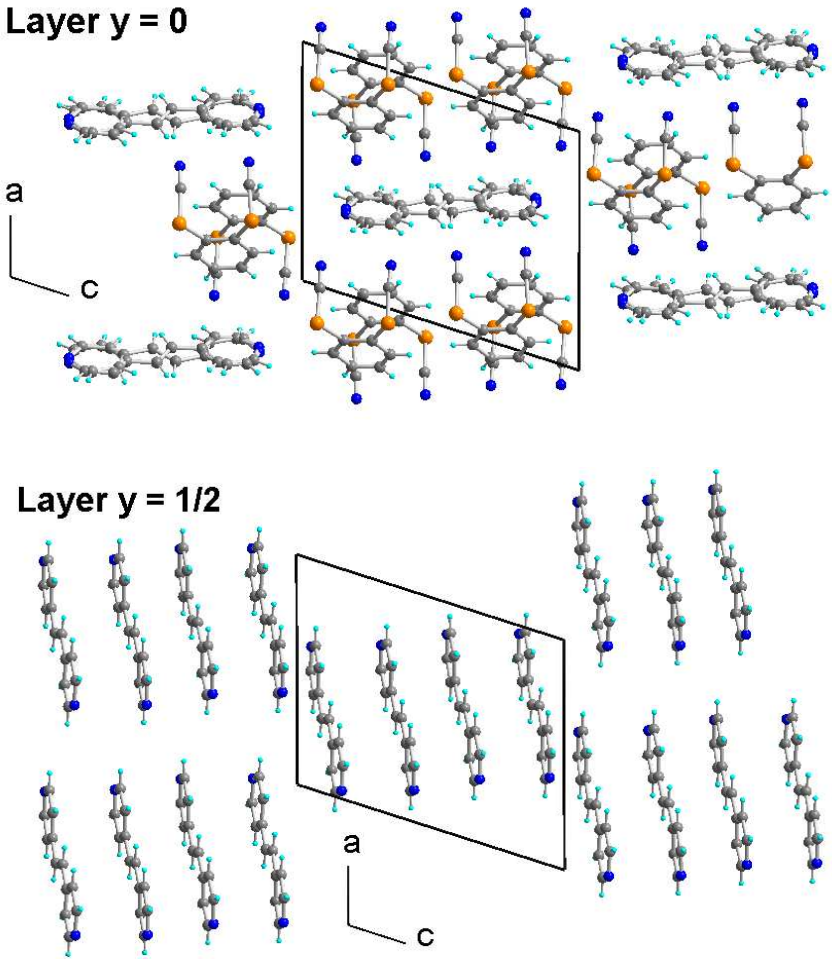


Figure S6 Illustration of the solid-state organization within the alternating layers in **(1)$_4$(bpen)$_5$**

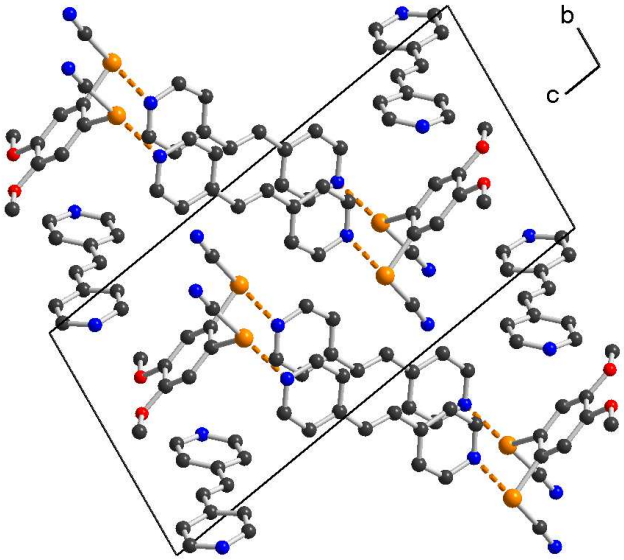


Figure S7 Projection view along *a* of the unit cell of **(3)(bpen)$_2$** before UV irradiation, showing the two crystallographically independent **bpen** molecules, one involved in ChB with **3** and the other interspersed between the dimethoxybenzene moieties. Hydrogen atoms were omitted for clarity.

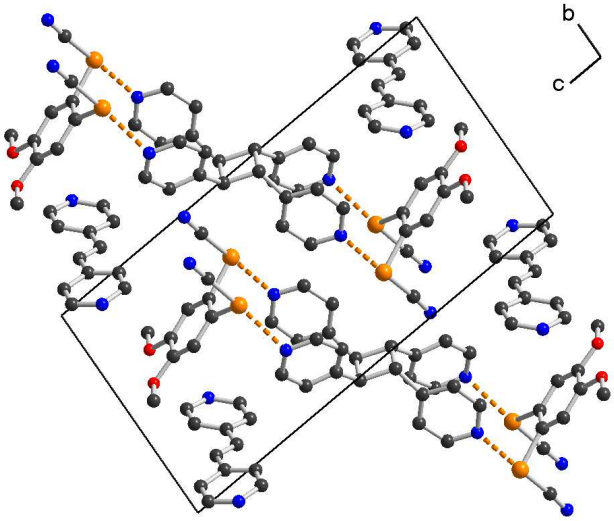


Figure S8 Projection view along *a* of the unit cell of **(3)(bpen)$_2$** after UV irradiation, showing the photo-cyclized **bpen** molecules involved in ChB with **3** and the other unmodified **bpen** molecule. Hydrogen atoms were omitted for clarity.