# Supporting Information

for

**Magnetic Ordering in a Vanadium-Organic Coordination Polymer Using a Pyrrolo[2,3-*d*:5,4-*d'*]bis(thiazole)-based Ligand**

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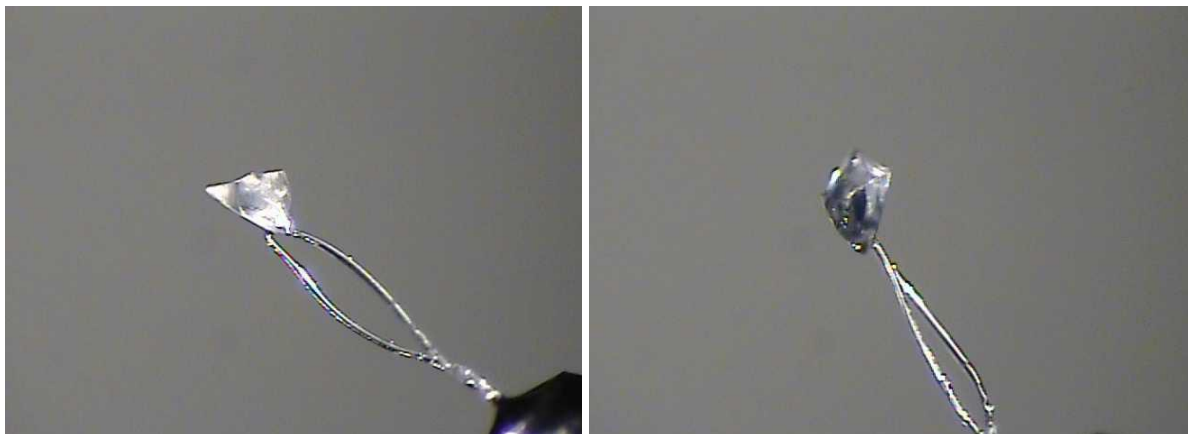*Chad Risko[b] and Ezekiel Johnston-Halperin[a]*

**Figure S1.** Photographs of single crystal of 4-hexyl-4*H*-pyrrolo[2,3-*d*:5,4-*d*']bis(thiazole) (**5**).
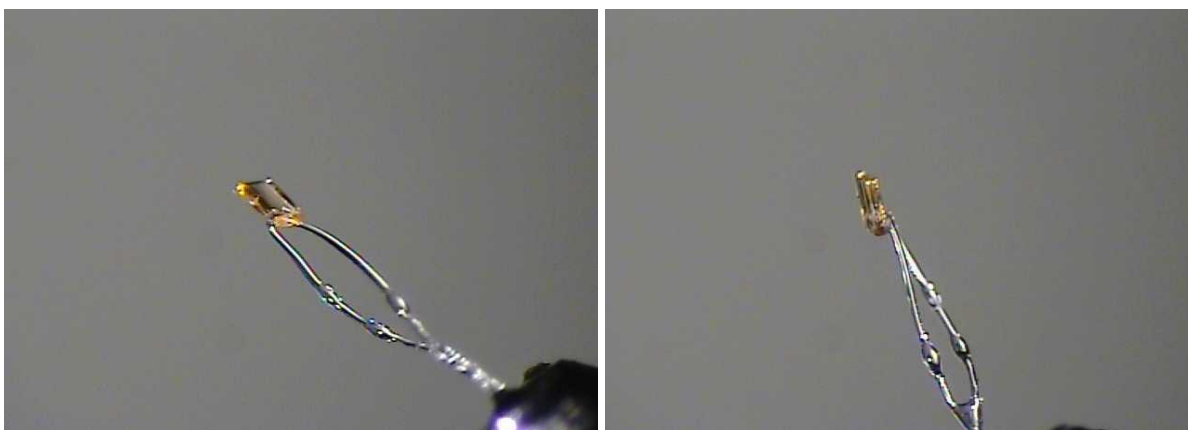


**Figure S2.** Photographs of a single crystal of 4-hexyl-2,6-diiodo-4*H*-pyrrolo[2,3-*d*:5,4-*d*']bis(thiazole) (**6**)
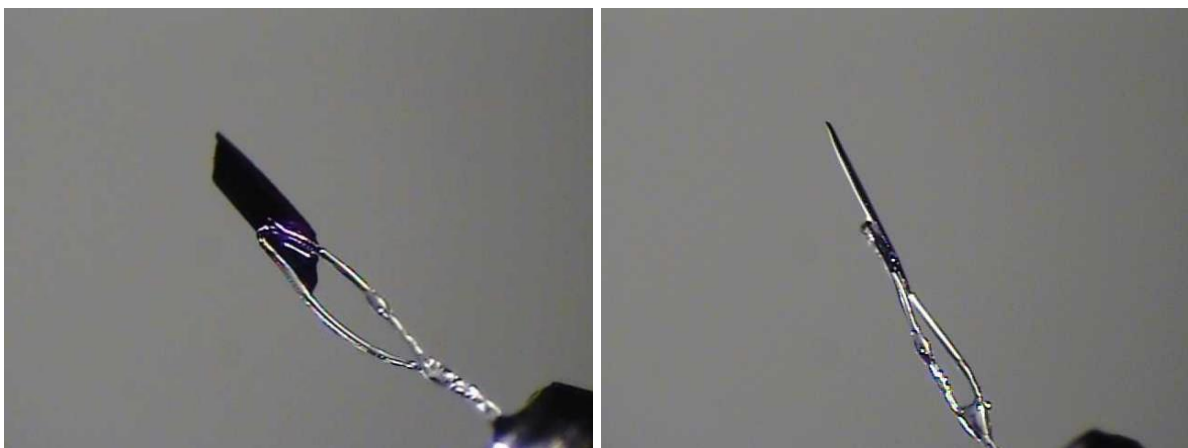


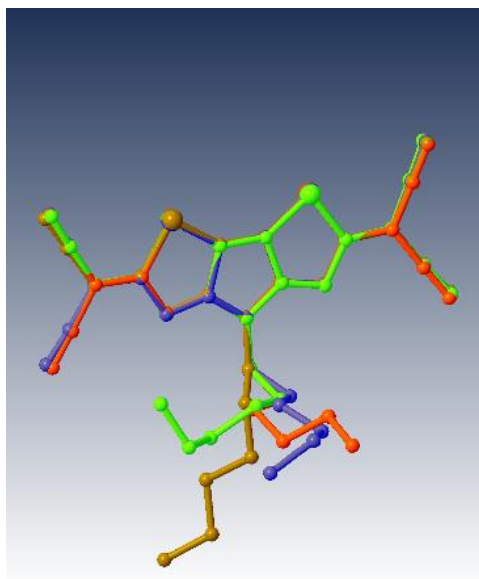**Figure S3.** Photographs of a single crystal of ligand **7**.

**Figure S4.** Overlay of the four independent molecules of compound **7** (1 is green; 1A is red; 1B is blue; 1C is brown).
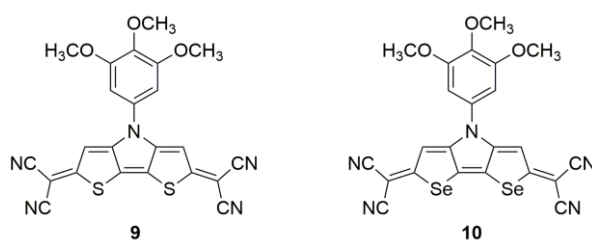


**Figure S5.** Structures of dithieno[3,2-*b*:2',3'-*d*]pyrrole (DTP) derivative (**9**) and diselenopheno[3,2-*b*:2',3'-*d*]pyrrole (DSP) derivative (**10**) investigated computationally.
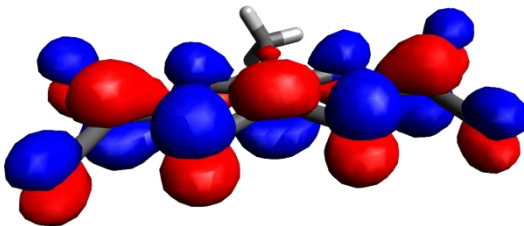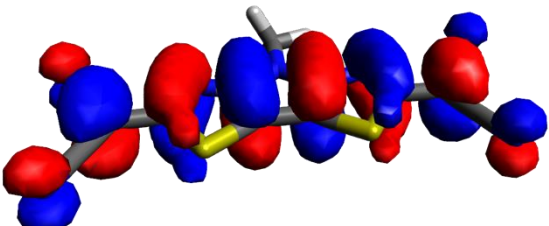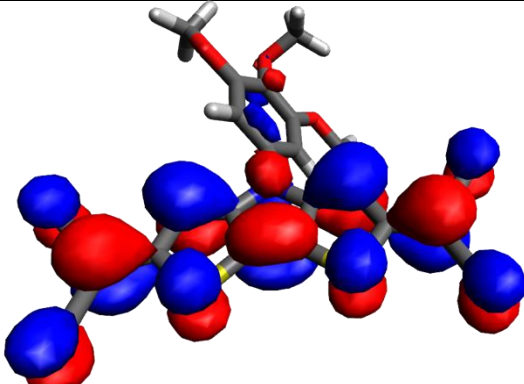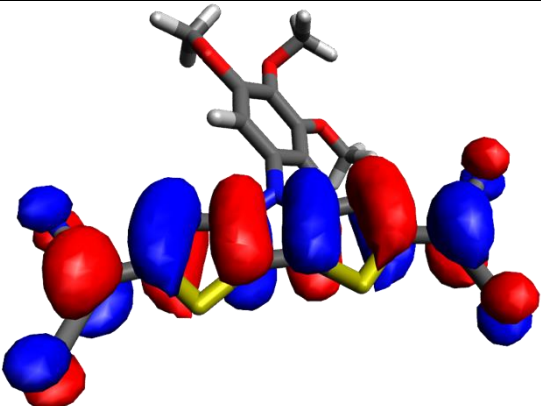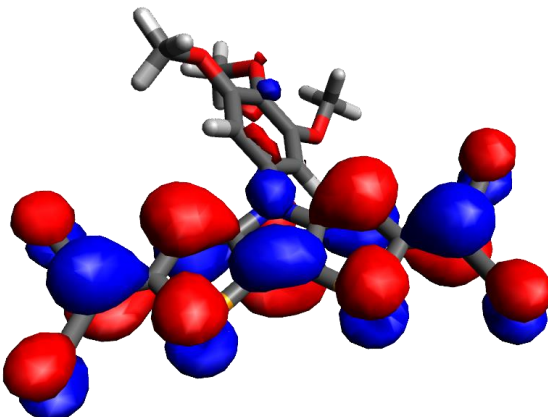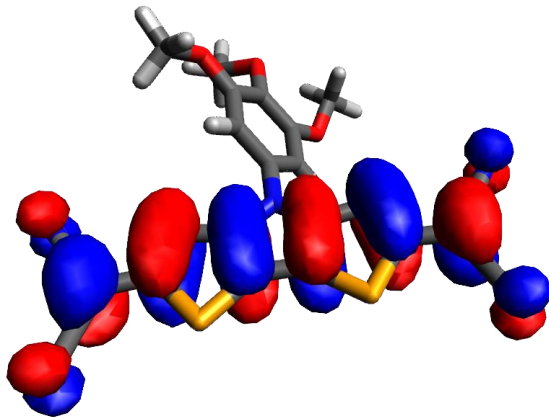
| | HOMO | LUMO |
|---|---|---|
| L7-methyl |  E = -9.31 eV |  E = -3.03 eV |
| 9 |  E = -8.55 eV |  E = -2.60 eV |
| 10 |  E = -8.51 eV |  E = -2.53 eV |

**Figure S6.** Pictorial representations and energies of the HOMO and LUMO for an *N*-methyl derivative of ligand **7** (**L7-methyl**), DTP derivative **9**, and DSP derivative (**10**) as determined at the OT-LC-ωPBE/cc-PVDZ level of theory.
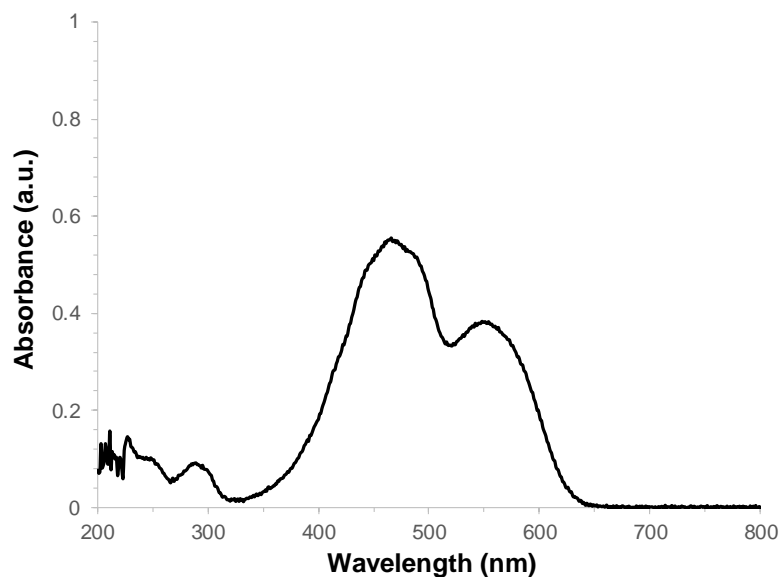
(a)
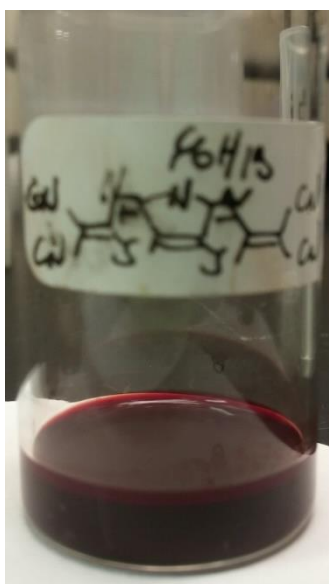


(b)
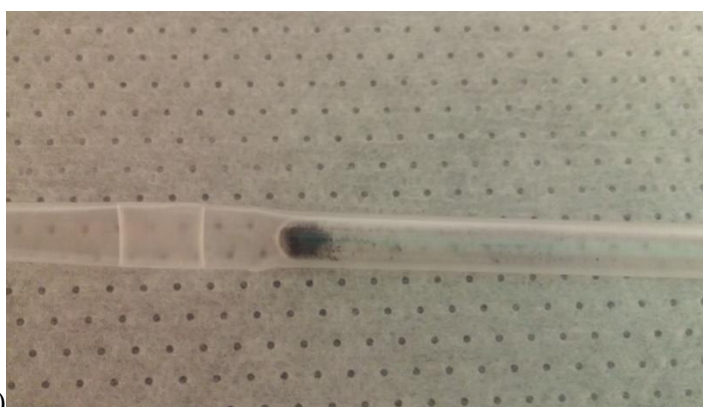


(c)

**Figure S7.**(*a*) UV-vis absorption spectra of ligand **7** in dichloromethane; (*b*) a photograph of a solution of ligand **7** in dichloromethane; (*c*) a photograph of the hybrid material **8** in a sealed quartz tube inside of a plastic straw.
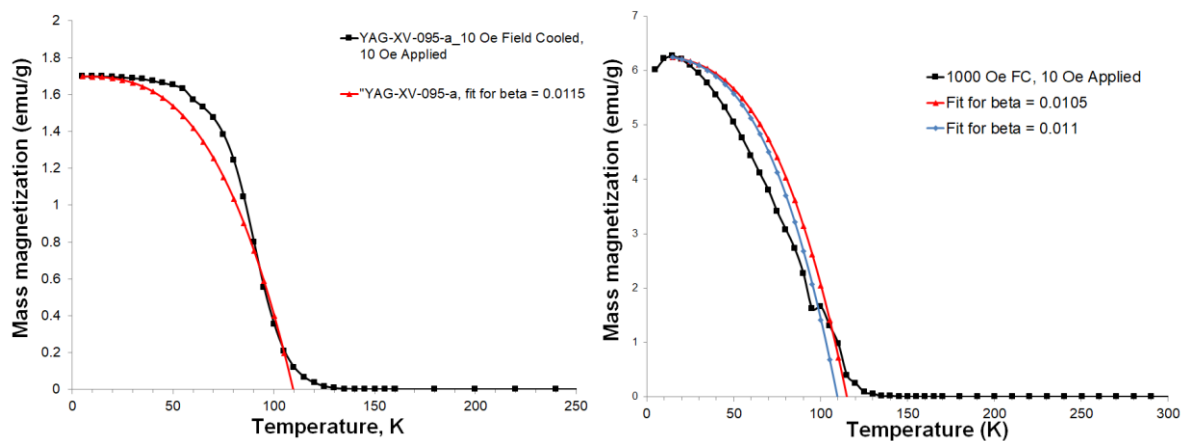
**Figure S8.** (*left*) Fit for the $\beta = 0.0115$ K$^{-3/2}$ for 1$^{st}$ batch YAG-XIV-095-a (estimated Curie temperature T$_C \sim 110$ K); (*right*) fit for the $\beta = 0.0105$ and $0.011$ K$^{-3/2}$ for 2$^{nd}$ batch of **8** (YAG-XVI-022-b; estimated Curie temperature T$_C \sim 115$ K and 110 K, respectively).
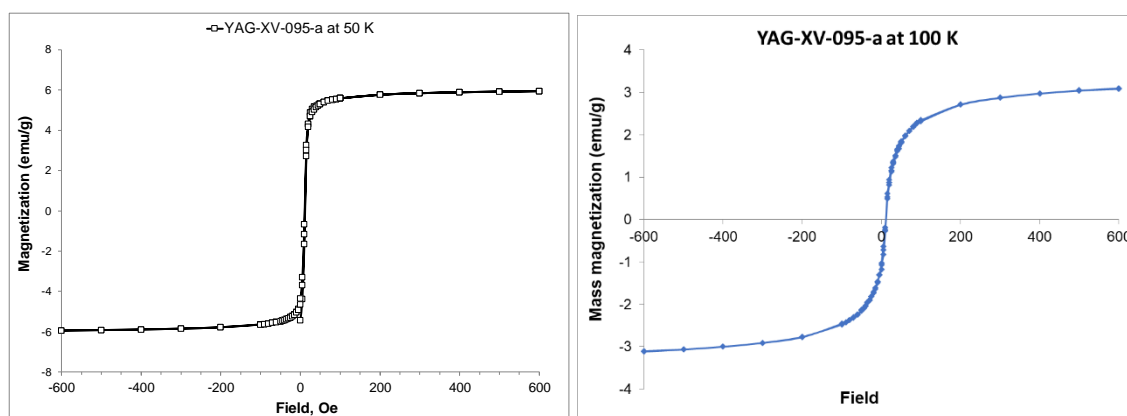


**Figure S9.** Hysteresis of **8** (first batch, YAG-XV-095-a) at (*left*) 50 K and (*right*) a 100 K.
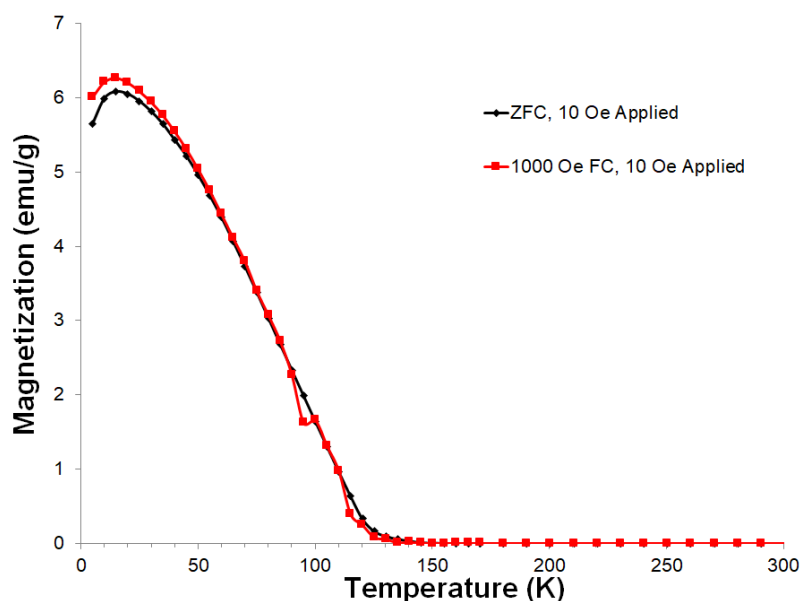
**Figure S10.** ZFC and FC temperature dependence of magnetization of material **8** (second independently prepared sample, YAG-XVI-022-b, ~1.1 mg of material **8** sealed in quartz tube).
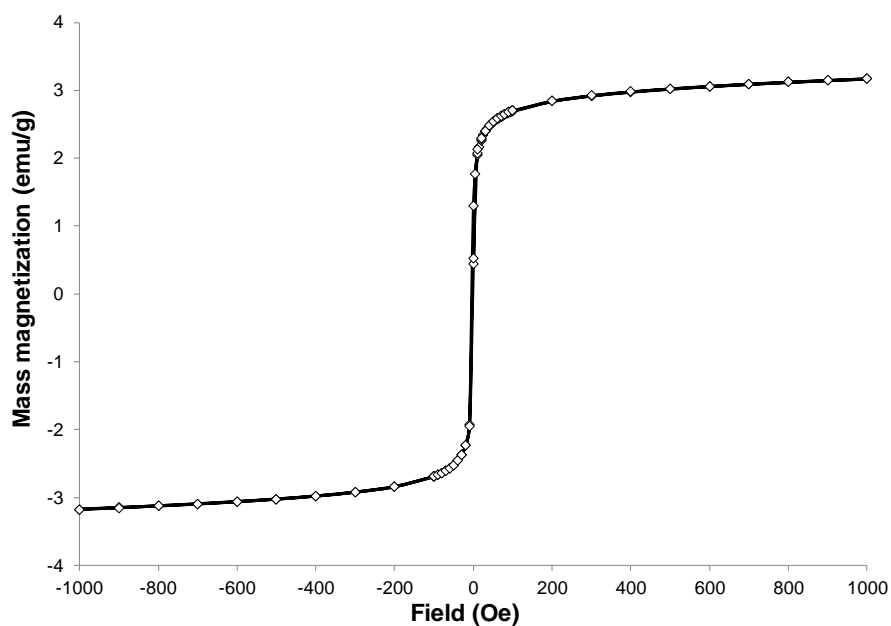


**Figure S11.** Hysteresis of **8** at 95 K (second independently prepared material, ~1.1 mg of YAG-XVI-022-b). Saturation magnetization is comparable to the 1st batch of **8** at 100 K (**Figure S9**, right).

**Figure S12.** Hysteresis of material **8** (*top*) at 5 K, (*bottom left*) at 50 K and (*bottom right*) at 95 K for a second independently prepared sample (batch YAG-XVI-022-b). Saturation magnetization reached 8.4 emu·g⁻¹ at 500 Oe at 5 K (comparable to 7.8 emu·g⁻¹ measured for the first batch YAG-XIV-095-a).

**Table S1.** X-ray data and processing parameters for compounds **5-7**.

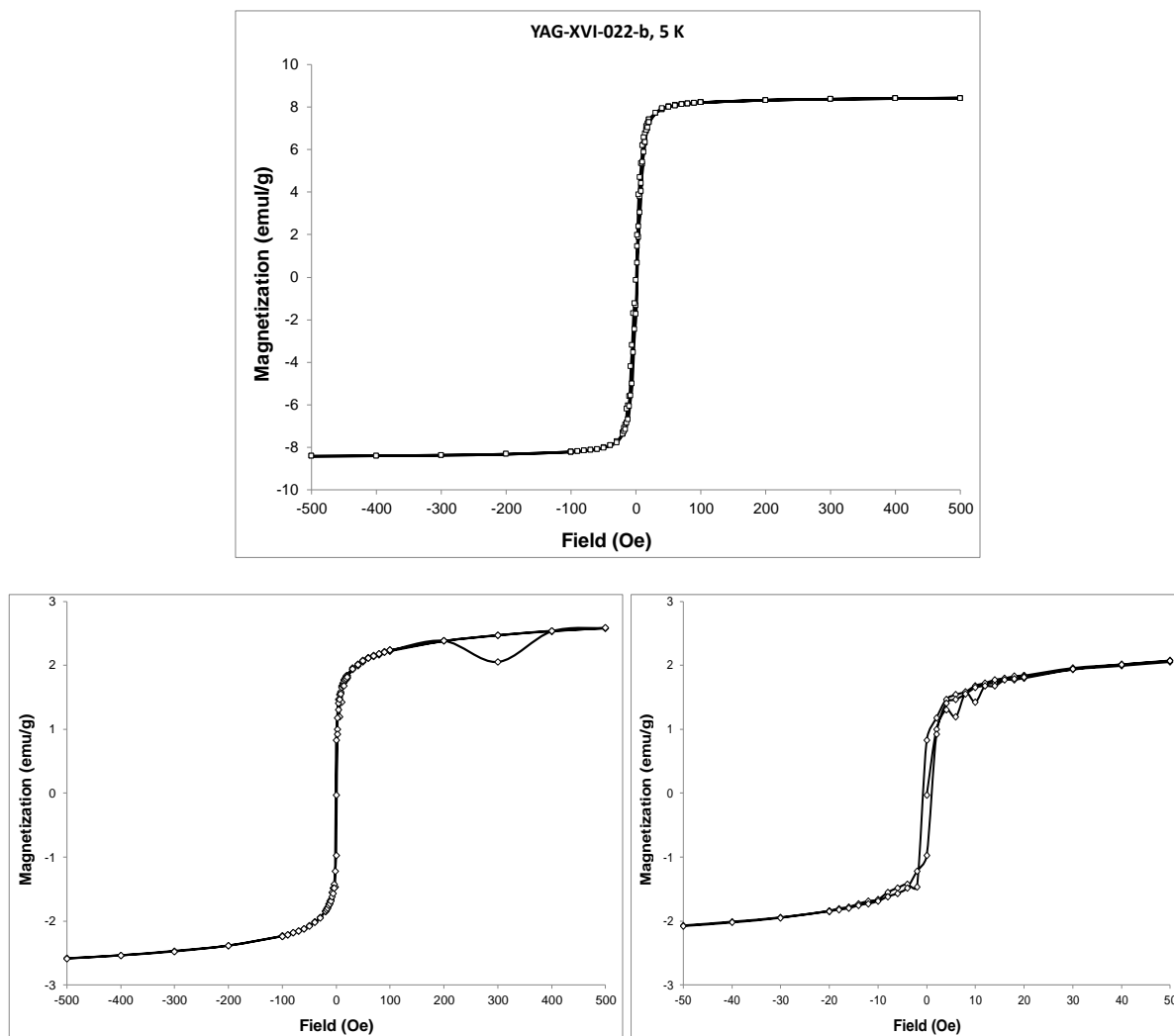| CCDC entry no. | 1819816 | 1819817 | 1868490 |
|---|---|---|---|
| Crystal system | Monoclinic | Monoclinic | Triclinic |
| Space group | *Cc* | *Cm* | P-1 |
| a, Å | 11.438(2) | 16.8767(2) | 15.8211(3) |
| b, Å | 11.940(2) | 33.8581(5) | 15.8245(3) |
| c, Å | 9.874(2) | 4.4165(1) | 16.6689(2) |
| α, deg | 90 | 90 | 79.740(1) |
| β, deg | 107.370(2) | 91.650(1) | 66.715(2) |
| γ, deg | 90 | 90 | 73.107(2) |
| V, Å$^3$ | 1287.0(4) | 2522.60(7) | 3658.41(12) |
| Mol formula | $C_{12}H_{15}N_3S_2$ | $C_{12}H_{13}I_2N_3S_2$ | $C_{18}H_{13}N_7S_2$ |
| fw | 265.39 | 517.17 | 391.47 |
| Formula units per cell (Z) | 4 | 6 | 8 |
| $D_{calcd}$ (Mg/m$^3$) | 1.370 | 2.043 | 1.422 |
| λ (Mo/Cu Kα), Å | 0.71073 | 0.71073 | 1.54184 |
| μ (mm$^{-1}$) | 0.395 | 3.979 | 2.794 |
| Absorption correction | Semi-empirical from equivalents | Semi-empirical from equivalents | Semi-empirical from equivalents |
| Total reflections | 6623 | 36525 | 48939 |
| Independent reflections | 2763 | 5624 | 14247 |
| $R_{int}$ | 0.0183 | 0.0237 | 0.0754 |
| Data/res/parameters | 2763 / 2 / 156 | 5624 / 5 / 260 | 14247 / 0 / 977 |
| R1[a] [I ≥ 2σ(I)] | 0.0203 | 0.0187 | 0.0468 |
| *w*R2[b] (all data) | 0.0509 | 0.0479 | 0.1199 |
| GOF on F$^2$ | 1.052 | 1.055 | 1.023 |
| Δρ(max), Δρ(min) (e/Å$^3$) | 0.141, -0.128 | 0.888, -0.681 | 0.583, -0.385 |

[a]$R1 = \Sigma\|F_o| - |F_c\|/\Sigma |F_o|$; [b]$R2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{\frac{1}{2}}$

**Table S2. Short intermolecular contacts between molecules of compound 7.**

| Molecules 1···1A/1C | Distance Å | Molecules 1B/1A···1C/1B | Distance Å |
|---|---|---|---|
| S(1)···S(2A) | 3.439(1) | S(1B)···S(2C) | 3.500(1) |
| S(1)···N(6A) | 2.974(2) | S(1B)···N(6C) | 2.993(2) |
| S(2)···N(6A) | 3.052(2) | S(2B)···N(6C) | 3.091(2) |
| N(4)···S(1A) | 3.070(2) | N(4B)···S(1C) | 3.125(2) |
| N(4)···S(2A) | 3.002(2) | S(2C)···N(4B) | 3.056(2) |
| C(2)···N(7C) | 3.006(2) | S(1A)···N(6B) | 3.325(2) |

**Table S3.** Comparison of the single-crystal X-ray structure for compound **7** and the OT-LC-ωPBE/cc-PVDZ optimized geometry for **L7-methyl**.

| | Compound 7 | | L7-methyl |
|---|---|---|---|
| Bond label | Distance (Å) | | Distance (Å) |
| C2-N2 | 1.369 | | 1.371 |
| C3-N2 | 1.378 | | 1.371 |
| C3-C5 | 1.467 | | 1.461 |
| C5-C6 | 1.352 | | 1.359 |
| C2-C6 | 1.463 | | 1.462 |
| N2-C13 | 1.473 | | 1.450 |
| C2-N1 | 1.300 | | 1.295 |
| N1-C1 | 1.378 | | 1.365 |
| C1-S1 | 1.786 | | 1.801 |
| S1-C6 | 1.712 | | 1.729 |
| C3-N3 | 1.294 | | 1.295 |
| N3-C4 | 1.381 | | 1.365 |
| C4-S2 | 1.776 | | 1.801 |
| S2-C5 | 1.720 | | 1.729 |
| | | | |
| Angle label | Bond angle (°) | | Bond angle (°) |
| C1-S1-C6 | 88.21 | | 87.90 |
| C4-S2-C5 | 87.98 | | 87.89 |
| C1-N1-C2 | 107.23 | | 108.66 |
| C3-N3-C4 | 107.26 | | 108.73 |

**Table S4.** Select information pertaining to the $S_0 \rightarrow S_1$ excitations as determined via TDDFT calculations at the OT-LC-ωPBE/cc-PVDZ level of theory.

| Molecule | E [eV] | λ [nm] | $f$ | Electronic Configuration | % contribution |
|---|---|---|---|---|---|
| **L7-methyl** | 2.26 | 549 | 0.37 | HOMO–1→LUMO; HOMO→LUMO | 43 56 |
| TCNQ | 3.13 | 396 | 1.08 | HOMO→LUMO | 100 |
| TCNE | 4.80 | 258 | 0.43 | HOMO→LUMO | 98 |
| TCNB | 4.62 | 268 | 0.04 | HOMO–1→LUMO; HOMO→LUMO+1 | 64 31 |
| **9** | 2.14 | 578 | 0.0036 | HOMO-3→LUMO; HOMO-2→LUMO; HOMO-1→LUMO | 37 7 54 |
| | 2.55 | 486 | 1.37 | HOMO→LUMO | 100 |
| **10** | 2.00 | 618 | 0.0104 | HOMO-3→LUMO; HOMO-2→LUMO; HOMO-1→LUMO | 33 6 58 |
| | 2.53 | 491 | 1.30 | HOMO→LUMO | 98 |