Supporting Information

Low-Coordinate Erbium(III) Single-Molecule Magnets with Photochromic Behavior

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Table S1. Selected crystallographic parameters for compounds 1 and 2.

| Compound | 1 | 1a | 2 |
|----------|---|----|---|
| Chemical formula | \([\text{Er}^{III}(\text{BHT})_3\text{dtepy}]_2\cdot 4\text{C}_4\text{H}_{12}\) | \([\text{Er}^{III}(\text{BHT})_3\text{dtepy}]_2\cdot 4\text{C}_4\text{H}_{12}\) | \([\text{Er}^{III}(\text{BHT})_3\text{azopy}]_2\cdot 2\text{C}_4\text{H}_{12}\) |
| CCDC deposition number | 2175717 | 2193239 | 2175718 |
| Instrument | Oxford Diffraction SuperNova | Oxford Diffraction SuperNova | Rigaku XtaLAB Synergy S |
| Radiation | Mo Kα (λ = 0.71073 Å) | Mo Kα (λ = 0.71073 Å) | Mo Kα (λ = 0.71073 Å) |
| Formula | C\(_{205}\)H\(_{287}\)Er\(_3\)F\(_{12}\)N\(_4\)O\(_9\)S\(_4\) | C\(_{205}\)H\(_{230}\)Er\(_3\)F\(_{12}\)N\(_4\)O\(_9\)S\(_4\) | C\(_{65}\)H\(_{101}\)ErN\(_4\)O\(_3\) |
| \(M_r\) / g mol\(^{-1}\) | 3809.39 | 3751.94 | 1153.75 |
| \(T\) / K | 130.0(1) | 270.0(1) | 100.00(13) |
| Crystal system | monoclinic | monoclinic | monoclinic |
| Space group | \(P2_1/c\) | \(P2_1/c\) | \(P2_1/c\) |
| \(a\) / Å | 14.3062(3) | 14.5311(2) | 12.66390(10) |
| \(b\) / Å | 24.9158(4) | 25.2122(4) | 27.17000(10) |
| \(c\) / Å | 55.6257(8) | 55.872(3) | 18.38180(10) |
| \(α\) / ° | 90 | 90 | 90 |
| \(β\) / ° | 95.5860(10) | 95.556(2) | 94.1770(10) |
| \(γ\) / ° | 90 | 90 | 90 |
| \(V\) / Å\(^3\) | 19733.6(6) | 20373.0(12) | 6307.98(7) |
| \(Z\) | 4 | 4 | 4 |
| \(ρ_{calc}\) / g cm\(^{-3}\) | 1.282 | 1.223 | 1.215 |
| \(μ\) / mm\(^{-1}\) | 1.373 | 1.330 | 1.375 |
| \(F(000)\) | 7972 | 7744 | 2444 |
| Crystal size / mm\(^3\) | 0.12 × 0.06 × 0.04 | 0.12 × 0.06 × 0.04 | 0.12 × 0.04 × 0.03 |
| θ range / ° | 2.545 – 28.753 (max) | 2.547 – 25.027 | 2.158 - 26.865 (max) |
| Reflections collected | 255 523 | 209 617 | 611 369 |
| Independent reflections | 47 624 | 35 921 | 13 567 |
| \(R_{int}\) | 0.1606 | 0.1693 | 0.0451 |
| Parameters/restraints | 2209/130 | 2199/199 | 842/180 |
| \(R\) [\(F_o > 2σ(F_o)\)] | 0.0770 | 0.0733 | 0.0487 |
| \(wR(F^2)\) | 0.1555 | 0.1997 | 0.1199 |
| GOF on \(F^2\) | 1.037 | 1.018 | 1.032 |
| \(Δρ_{max}, Δρ_{min}\) / e Å\(^{-3}\) | 2.063/-1.200 | 1.928/-0.999 | 2.289/-3.580 |
| Completeness / % | 92.9 | 99.8 | 99.9 |
Figure S1. Packing diagram showing the crystal structure of 1 along the \(a\) (a), \(b\) (b) and \(c\) (c) crystallographic direction and the shortest intermolecular Er···Er distance of 13.437 Å. BHT ligands and H-atoms are omitted for clarity. Er – green balls.
Figure S2. Packing diagram showing the crystal structure of 2 along the a (a), b (b) and c (c) crystallographic direction and the shortest intermolecular Er···Er distance of 11.040 Å. BHT ligands and H-atoms are omitted for clarity. Er – green balls, O – red balls, C – gray balls, N – light blue balls.
Figure S3. In-phase ($\chi'$) and out-of-phase ($\chi''$) AC susceptibilities for 1 at 2.5 K measured in the 0-5000 Oe magnetic field range (a) and at 800 Oe in the 2.2-6.4 K temperature range (b). Values of $\alpha$ and $\tau$ parameters are gathered in Table S2. The solid lines are the best fits to generalized Debye model.
Table S2. Values of $\alpha$ and $\tau$ parameters obtained from generalized Debye model fitting of the $\tau(\nu)$ dependences for 1 at 2.5 K measured in the 0-5000 Oe magnetic field range depicted in Figure S3a (columns 1-5) and at 800 Oe in the 2.2-6.4 K temperature range depicted in Figure S3b (columns 6-10).

| $H$ (Oe) | $T = 2.5$ K (Figure S3a) | $H = 800$ Oe (Figure S3b) |
|----------|--------------------------|--------------------------|
|          | $\alpha$ | $sd$ | $\tau$ (s) | $sd$ | $T$ (K) | $\alpha$ | $sd$ | $\tau$ (s) | $sd$ | $T$ (K) |
| 0        | 0.00     | 0.0603 | $6.68 \times 10^{-5}$ | 2.63 | $10^{-5}$ | 2.2 | 0.380 | 0.002 | $5.56 \times 10^{-2}$ | 5.1 | $10^{-4}$ |
| 50       | 0.00     | 0.5236 | $5.5066 \times 10^{-5}$ | 8.02 | $10^{-5}$ | 2.3 | 0.372 | 0.003 | $4.43 \times 10^{-2}$ | 4.9 | $10^{-4}$ |
| 100      | 0.0894   | 0.4801 | $1.0326 \times 10^{-5}$ | 6.45 | $10^{-5}$ | 2.4 | 0.364 | 0.003 | $3.60 \times 10^{-2}$ | 4.6 | $10^{-4}$ |
| 150      | 0.2430   | 0.4461 | $6.1786 \times 10^{-5}$ | 6.79 | $10^{-5}$ | 2.6 | 0.351 | 0.005 | $2.46 \times 10^{-2}$ | 4.2 | $10^{-4}$ |
| 200      | 0.3151   | 0.2394 | $2.3266 \times 10^{-4}$ | 1.5 | $10^{-4}$ | 2.8 | 0.338 | 0.007 | $1.74 \times 10^{-2}$ | 3.5 | $10^{-4}$ |
| 300      | 0.3371   | 0.0274 | $0.00258$ | 0.00119 | 3.0 | 0.321 | 0.008 | $1.25 \times 10^{-2}$ | 2.8 | $10^{-4}$ |
| 400      | 0.3623   | 0.0210 | $0.0045$ | 0.00177 | 3.2 | 0.303 | 0.009 | $9.1 \times 10^{-3}$ | 2.1 | $10^{-4}$ |
| 500      | 0.342    | 0.007 | $1.82 \times 10^{-2}$ | 3.74 | $10^{-2}$ | 3.4 | 0.28 | 0.01 | $6.8 \times 10^{-3}$ | 1.5 | $10^{-4}$ |
| 600      | 0.345    | 0.006 | $2.30 \times 10^{-2}$ | 4.36 | $10^{-2}$ | 3.6 | 0.261 | 0.009 | $5.1 \times 10^{-3}$ | 1.1 | $10^{-4}$ |
| 700      | 0.352    | 0.005 | $2.69 \times 10^{-2}$ | 4.98 | $10^{-2}$ | 4.0 | 0.226 | 0.008 | $2.87 \times 10^{-2}$ | 4.9 | $10^{-3}$ |
| 800      | 0.31     | 0.04 | $2.89 \times 10^{-2}$ | 1.8 | $10^{-3}$ | 4.4 | 0.205 | 0.005 | $1.65 \times 10^{-2}$ | 2.7 | $10^{-3}$ |
| 1000     | 0.35     | 0.02 | $3.34 \times 10^{-2}$ | 1.5 | $10^{-3}$ | 4.8 | 0.195 | 0.008 | $9.5 \times 10^{-4}$ | 1.8 | $10^{-5}$ |
| 1200     | 0.36     | 0.08 | $3.15 \times 10^{-2}$ | 8.3 | $10^{-3}$ | 5.2 | 0.190 | 0.009 | $5.7 \times 10^{-4}$ | 1.4 | $10^{-5}$ |
| 1400     | 0.33     | 0.04 | $2.13 \times 10^{-2}$ | 3.7 | $10^{-3}$ | 5.6 | 0.18 | 0.01 | $3.7 \times 10^{-4}$ | 1.2 | $10^{-5}$ |
| 1600     | 0.31     | 0.02 | $1.51 \times 10^{-2}$ | 9.82 | $10^{-4}$ | 6.0 | 0.15 | 0.01 | $2.8 \times 10^{-4}$ | 1.2 | $10^{-5}$ |
| 1800     | 0.30     | 0.02 | $1.17 \times 10^{-2}$ | 5.56 | $10^{-4}$ | 6.4 | 0.10 | 0.01 | $2.38 \times 10^{-4}$ | 9.5 | $10^{-6}$ |
| 2000     | 0.36     | 0.004 | $1.09 \times 10^{-2}$ | 3.59 | $10^{-4}$ | 6.8 | 0.28 | 0.01 | $6.8 \times 10^{-3}$ | 1.5 | $10^{-4}$ |
| 2500     | 0.32     | 0.003 | $5.06 \times 10^{-3}$ | 9.58 | $10^{-5}$ | 7.0 | 0.26 | 0.01 | $5.1 \times 10^{-3}$ | 1.1 | $10^{-4}$ |
| 3000     | 0.32     | 0.01 | $2.48 \times 10^{-3}$ | 9.99 | $10^{-5}$ | 7.0 | 0.26 | 0.01 | $5.1 \times 10^{-3}$ | 1.1 | $10^{-4}$ |
| 4000     | 0.33     | 0.01 | $7.62 \times 10^{-4}$ | 1.79 | $10^{-4}$ | 7.0 | 0.26 | 0.01 | $5.1 \times 10^{-3}$ | 1.1 | $10^{-4}$ |
| 5000     | 0.36     | 0.02 | $2.58 \times 10^{-4}$ | 1.87 | $10^{-4}$ | 7.0 | 0.26 | 0.01 | $5.1 \times 10^{-3}$ | 1.1 | $10^{-4}$ |

Table S3. Values of the best-fit parameters obtained by fitting the $\tau^{-1}(H)$ using Eq. 1 (top part of the table) and the $\tau(T)$ using Eq. 2 (bottom part of the table) for compound 1. The relevant fits are shown as black lines in Figure 10a and 10c in the main text, respectively.

$$\tau^{-1}(H) = A_1/(1 + A_2H^2) + B_1H^4 + D$$
(Eq. 1)

$$\ln(\tau^{-1}) = \ln[(A + B_1T + CT^2 + \tau_0^2\exp(-U_{eff}/k_BT)]^{-1}$$
(Eq. 2)

| Magnetic field dependence (black line in Figure 10a) |
|--------------------------|
| $T$ (K) | 2.5 K |
| Frequency range (Hz) | 1-1000 |
| Field range (Oe) | 0-5000 |
| $A_1$ (s$^{-1}$) | 10195(15399) |
| $A_2$ (Oe$^{-2}$) | 0.00116(183) |
| $B_1$ (Oe$^{-4}$) | 4.8(2)$ \times 10^{-12}$ |
| $D$ (s$^{-1}$) | 18(3) |
| $R^2$ | 0.948 |

| Temperature dependence (black line in Figure 10c) |
|--------------------------|
| $H_{oc}$ (Oe) | 800 |
| Frequency range (Hz) | 1-1000 |
| Temperature range (K) | 2.2-6.4 |
| $A$ (s$^{-1}$) | 0 (fixed) |
| $B_1$ (s$^{-1}$ K$^{-1}$ Oe$^{-1}$) | 0.788 (fixed) |
| $C$ (s$^{-1}$ K$^{-n}$) | 0.34(1) |
| $n$ | 4.92(4) |
| $R^2$ | 0.9999 |
Figure S4. In-phase ($\chi'$) and out-of-phase ($\chi''$) AC susceptibilities for 1UV at 2.5 K measured in the 0-5000 Oe magnetic field range (a) and at 1000 Oe in the 1.8-6.4 K temperature range (b). Values of $\alpha$ and $\tau$ parameters are gathered in Table S3. The solid lines are the best fits to generalized Debye model.
The relevant fits are shown as blue (and the Table S5. Values of the best-fit parameters obtained by fitting the \( \tau(\nu) \) dependences for \( \text{1UV} \) at 2.5 K measured in the 0-5000 Oe magnetic field range depicted in Figure S4a (columns 1-5) and at 1000 Oe in the 1.8-6.4 K temperature range depicted in Figure S4b (columns 6-10).

| \( T = 2.5 \text{ K (Figure S4a)} \) | \( H = 1000 \text{ Oe (Figure S4b)} \) |
|----------------|----------------|
| \( H \) (Oe) | \( \alpha \) | \( \sigma \) | \( \tau \) (s) | \( \sigma \) | \( T \) (K) | \( \alpha \) | \( \sigma \) | \( \tau \) (s) | \( \sigma \) |
| 0   | 0.07 | 1.1 \times 10^{-4} | 3.3 \times 10^{-5} | 1.8 | 0.53 | 0.02 | 0.10 | 2.3 \times 10^{-2} |
| 50  | 0.130 | 4.3 \times 10^{-4} | 2.2 \times 10^{-5} | 1.9 | 0.53 | 0.01 | 9.2 \times 10^{-2} | 7.6 \times 10^{-3} |
| 100 | 0.133 | 2.5 \times 10^{-4} | 1.0 \times 10^{-5} | 2.0 | 0.52 | 0.01 | 6.9 \times 10^{-2} | 4.8 \times 10^{-3} |
| 150 | 0.175 | 4.0 \times 10^{-4} | 7.2 \times 10^{-6} | 2.1 | 0.52 | 0.01 | 5.4 \times 10^{-2} | 3.4 \times 10^{-3} |
| 200 | 0.258 | 7.0 \times 10^{-4} | 1.3 \times 10^{-5} | 2.2 | 0.51 | 0.01 | 4.3 \times 10^{-2} | 2.3 \times 10^{-3} |
| 300 | 0.411 | 2.3 \times 10^{-3} | 2.1 \times 10^{-5} | 2.3 | 0.50 | 0.01 | 3.5 \times 10^{-2} | 1.7 \times 10^{-3} |
| 400 | 0.450 | 2.4 \times 10^{-3} | 1.6 \times 10^{-4} | 2.4 | 0.49 | 0.01 | 2.9 \times 10^{-2} | 1.3 \times 10^{-3} |
| 600 | 0.458 | 2.2 \times 10^{-2} | 3.5 \times 10^{-4} | 2.6 | 0.48 | 0.01 | 2.0 \times 10^{-2} | 8.3 \times 10^{-3} |
| 700 | 0.470 | 1.4 \times 10^{-2} | 5.4 \times 10^{-3} | 2.8 | 0.45 | 0.01 | 1.4 \times 10^{-2} | 5.4 \times 10^{-4} |
| 800 | 0.474 | 1.2 \times 10^{-2} | 7.1 \times 10^{-4} | 3.0 | 0.43 | 0.01 | 1.0 \times 10^{-2} | 3.6 \times 10^{-4} |
| 1000| 0.485 | 2.4 \times 10^{-2} | 1.1 \times 10^{-3} | 3.2 | 0.40 | 0.01 | 7.6 \times 10^{-3} | 2.5 \times 10^{-4} |
| 1200| 0.486 | 2.0 \times 10^{-3} | 1.4 \times 10^{-3} | 3.4 | 0.37 | 0.01 | 5.8 \times 10^{-3} | 1.7 \times 10^{-4} |
| 1400| 0.485 | 3.2 \times 10^{-3} | 1.5 \times 10^{-3} | 3.6 | 0.35 | 0.01 | 4.4 \times 10^{-3} | 1.2 \times 10^{-4} |
| 1600| 0.481 | 0.03075 | 1.4 \times 10^{-3} | 4.0 | 0.30 | 0.01 | 2.5 \times 10^{-3} | 6.4 \times 10^{-5} |
| 1800| 0.472 | 0.0275 | 1.2 \times 10^{-3} | 4.4 | 0.27 | 0.01 | 1.6 \times 10^{-3} | 3.9 \times 10^{-5} |
| 2000| 0.472 | 0.02511 | 9.5 \times 10^{-4} | 4.8 | 0.25 | 0.01 | 9.6 \times 10^{-4} | 2.7 \times 10^{-3} |
| 2500| 0.43 | 1.4 \times 10^{-2} | 1.4 \times 10^{-2} | 5.2 | 0.22 | 0.01 | 6.3 \times 10^{-4} | 2.0 \times 10^{-3} |
| 3000| 0.45 | 6.9 \times 10^{-3} | 1.2 \times 10^{-3} | 5.6 | 0.20 | 0.01 | 4.4 \times 10^{-4} | 1.6 \times 10^{-3} |
| 4000| 0.41 | 1.8 \times 10^{-3} | 6.5 \times 10^{-5} | 6.0 | 0.15 | 0.01 | 3.5 \times 10^{-4} | 1.3 \times 10^{-5} |
| 5000| 0.41 | 7.6 \times 10^{-4} | 2.2 \times 10^{-4} | 6.4 | 0.10 | 0.01 | 2.96 \times 10^{-4} | 9.5 \times 10^{-6} |

Table S5. Values of the best-fit parameters obtained by fitting the \( \tau^{-1}(H) \) using Eq. 1 (top part of the table) and the \( \tau(T) \) using Eq. 2 (bottom part of the table) for compound \( \text{1UV} \). The relevant fits are shown as blue lines in Figure 10a and 10c in the main text, respectively.

\[
\tau^{-1}(H) = A_1/(1 + A_2 H^2) + B_1 H^4 + D \\
\ln(T^{-1}) = \ln[(A + B_2 T + C T^n + D)^{-1}] \\
\]

(Eq. 1)

(Magnetic field dependence (blue line in Figure 10a))

| Temperature range (K) | Frequency range (Hz) | Field range (Oe) |
|----------------------|----------------------|-----------------|
| 1.8-6.4              | 1-1000               | 0-5000          |

| \( H_{\text{DC}} \) (Oe) | \( A_1 \) (s\(^{-1}\)) | \( A_2 \) (s\(^{-1}\)Oe\(^{-2}\)) | \( B_1 \) (Oe\(^{-4}\)) | \( R^2 \) |
|-------------------------|----------------------|-----------------|----------------|--------|
| 1000                    | 26320(17185)         | 6(4) \times 10^{-4} | 2.1(3)-10\(^{-12}\) | 0.905  |

| Temperature dependence (blue line in Figure 10c) |
|---------------------------------------------|
| \( T \) (K) | \( H_{\text{DC}} \) (Oe) | \( A \) (s\(^{-1}\)) | \( B_2 \) (s\(^{-1}\) K\(^{-1}\) Oe\(^{-1}\)) | \( C \) (s\(^{-1}\) K\(^{-n}\)) | \( n \) | \( R^2 \) |
| 2.5 | 1000 | 0 (fixed) | 0.8206 (fixed) | 0.68(16) | 4.3(3) | 0.99882 |

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Figure S5. In-phase ($\chi'$) and out-of-phase ($\chi''$) AC susceptibilities for 1vis at 2.5 K measured in the 0-5000 Oe magnetic field range (a) and at 1000 Oe in the 1.8-6.4 K temperature range (b). Values of $\alpha$ and $\tau$ parameters are gathered in Table S6. The solid lines are the best fits to generalized Debye model.
Table S6. Values of $\tau$ parameters obtained from generalized Debye model fitting of the $\tau(\nu)$ dependences for 1vis at 2.5 K measured in the 0-5000 Oe magnetic field range depicted in Figure S5a (columns 1-5) and at 1000 Oe in the 1.8-6.4 K temperature range depicted in Figure S5b (columns 6-10).

| $H$ (Oe) | $T$ (K) | $\alpha$ | $sd$ | $\tau$ (s) | $sd$ | $H$ (1000 Oe) | $T$ (K) | $\alpha$ | $sd$ | $\tau$ (s) | $sd$ |
|----------|---------|----------|------|------------|------|-------------|---------|----------|------|------------|------|
| 50       | 1.8     | 0.09     | 0.04 | 1.3-10^{-4} | 2.2-10^{-5} | 0.52 | 0.02 | 0.1 | 2.5-10^{-4} | 1.9 |
| 100      | 1.9     | 0.13     | 0.02 | 2.4-10^{-4} | 1.1-10^{-5} | 0.52 | 0.01 | 8.5-10^{-2} | 8.1-10^{-3} | 1.0 |
| 150      | 2.0     | 0.165    | 0.008 | 4.0-10^{-4} | 8.7-10^{-6} | 0.51 | 0.01 | 6.6-10^{-2} | 5.3-10^{-3} | 1.1 |
| 200      | 2.1     | 0.248    | 0.007 | 7.0-10^{-4} | 1.4-10^{-5} | 0.51 | 0.01 | 5.2-10^{-2} | 3.7-10^{-3} | 1.2 |
| 300      | 2.2     | 0.39     | 0.01 | 2.14-10^{-3} | 7.4-10^{-5} | 0.50 | 0.01 | 4.3-10^{-3} | 2.7-10^{-5} | 1.3 |
| 400      | 2.3     | 0.43     | 0.01 | 4.9-10^{-3} | 1.6-10^{-4} | 2.3  | 0.01 | 3.6-10^{-3} | 2.1-10^{-5} | 1.4 |
| 600      | 2.4     | 0.44     | 0.01 | 8.0-10^{-3} | 2.7-10^{-4} | 2.4  | 0.01 | 2.9-10^{-4} | 1.5-10^{-4} | 1.5 |
| 700      | 2.5     | 0.44     | 0.01 | 1.98-10^{-2} | 4.3-10^{-4} | 2.6  | 0.01 | 2.05-10^{-2} | 9.5-10^{-4} | 1.6 |
| 800      | 2.6     | 0.45     | 0.01 | 1.46-10^{-2} | 7.0-10^{-4} | 2.8  | 0.01 | 1.47-10^{-2} | 6.1-10^{-4} | 1.7 |
| 1000     | 2.7     | 0.46     | 0.01 | 1.99-10^{-2} | 1.1-10^{-3} | 3.0  | 0.01 | 1.07-10^{-2} | 4.0-10^{-4} | 1.8 |
| 1200     | 2.8     | 0.45     | 0.02 | 2.1-10^{-2} | 1.4-10^{-3} | 3.2  | 0.01 | 7.9-10^{-3} | 2.7-10^{-4} | 1.9 |
| 1400     | 2.9     | 0.45     | 0.02 | 2.4-10^{-2} | 1.8-10^{-3} | 3.4  | 0.01 | 6.0-10^{-3} | 1.8-10^{-4} | 2.0 |
| 1600     | 3.0     | 0.43     | 0.02 | 2.6-10^{-2} | 2.6-10^{-3} | 3.6  | 0.01 | 4.5-10^{-3} | 1.3-10^{-4} | 2.1 |
| 1800     | 3.1     | 0.43     | 0.02 | 2.5-10^{-2} | 2.6-10^{-3} | 4.0  | 0.01 | 2.66-10^{-3} | 6.3-10^{-5} | 2.2 |
| 2000     | 3.2     | 0.42     | 0.03 | 2.4-10^{-2} | 2.5-10^{-3} | 4.4  | 0.01 | 1.58-10^{-3} | 3.7-10^{-5} | 2.3 |
| 2500     | 3.4     | 0.43     | 1.02 | 1.64-10^{-2} | 4.37-10^{-4} | 4.8  | 0.01 | 9.7-10^{-4} | 2.4-10^{-4} | 2.4 |
| 3000     | 3.5     | 0.49     | 0.39 | 1.22-10^{-2} | 1.96-10^{-4} | 5.2  | 0.01 | 6.2-10^{-4} | 1.8-10^{-4} | 2.5 |
| 4000     | 3.6     | 0.50     | 0.05 | 2.58-10^{-3} | 1.14-10^{-4} | 5.6  | 0.01 | 4.3-10^{-4} | 1.7-10^{-4} | 2.6 |
| 5000     | 3.7     | 0.46     | 0.08 | 6.86-10^{-4} | 1.69-10^{-4} | 6.0  | 0.01 | 3.4-10^{-4} | 1.4-10^{-5} | 2.7 |
|          |         |          |      |             |       | 6.4  | 0.14 | 2.4-10^{-4} | 1.6-10^{-5} | 2.8 |

Table S7. Values of the best-fit parameters obtained by fitting the $\tau^{-1}(H)$ using Eq. 1 (top part of the table) and the $\tau(T)$ using Eq. 2 (bottom part of the table) for compound 1vis. The relevant fits are shown as red lines in Figure 10a and 10c in the main text, respectively.

$t^{-1}(H) = A_1/(1 + A_2 H^2) + B_1 H^4 + D$ (Eq. 1)

$\ln(\tau^{-1}) = \ln([A + B_2 T + C T^n + \tau_0^{-1} \exp(-U_{eff}/k_B T)]^{-1})$ (Eq. 2)

| Magnetic field dependence (red line in Figure 10a) | Temperature dependence (red line in Figure 10c) |
|--------------------------------------------------|-----------------------------------------------|
| $T$ (K)                                          | $H_{dc}$ (Oe)                                  |
| 2.5 K                                            | 1000                                           |
| Frequency range (Hz)                             | Frequency range (Hz)                           |
| 1-1000                                          | 1-1000                                        |
| Field range (Oe)                                | Temperature range (K)                          |
| 0-5000                                          | 1.8-6.4                                       |
| $A_1$ (s^{-1})                                  | $A$ (s^{-1})                                    |
| 63288                                           | 0 (fixed)                                      |
| $A_2$ (Oe^{-2})                                 | $B_2$ (s^{-2} K^{-1} Oe^{-1})                  |
| 0.0016(10)                                      | 1.03 (fixed)                                   |
| $B_1$ (Oe^{-4})                                 | $C$ (s^{-1} K^{-1})                            |
| 2.6(12) \times 10^{-12}                         | 0.60(8)                                        |
| $D$ (s^{-3})                                    | $n$                                            |
| 1.14 \times 10^{-3} (fixed)                     | 4.49(15)                                       |
| $R^2$                                           | $R^2$                                          |
| 0.878                                           | 0.999                                          |
Figure S6. In-phase ($\chi'$) and out-of-phase ($\chi''$) AC susceptibilities for 2 at 1.8 K measured in the 100-5000 Oe magnetic field range (a), at 500 Oe in the 1.8-3.4 K temperature range (b) and at 2000 Oe in the 1.8-3.6 K temperature range. Values of $\alpha$ and $\tau$ parameters are gathered in Table S8 (a) and S9 (b and c). The solid lines are the best fits to generalized Debye model.
Table S8. Values of $\alpha$ and $\tau$ parameters obtained from generalized Debye model fitting of the $\tau(\nu)$ dependences for 2 at 1.8 K measured in the 100-5000 Oe magnetic field range depicted in Figure S6a.

| $H$ (Oe) | $\alpha$ | sd | $\tau$ (s) | sd |
|----------|----------|----|------------|----|
| 100      | 0.1825   | 0.0216 | 0.0069     | 0.0009 |
| 200      | 0.1802   | 0.0066 | 0.00167    | 0.00003 |
| 300      | 0.2206   | 0.0068 | 0.00284    | 0.00005 |
| 400      | 0.2466   | 0.0069 | 0.00392    | 0.00007 |
| 500      | 0.2691   | 0.0061 | 0.00500    | 0.00007 |
| 600      | 0.2869   | 0.0060 | 0.00610    | 0.00009 |
| 700      | 0.3077   | 0.0063 | 0.00728    | 0.00011 |
| 800      | 0.3291   | 0.0069 | 0.00856    | 0.00016 |
| 1000     | 0.3770   | 0.0083 | 0.01173    | 0.00030 |

$T = 1.8$ K (Figure S6a)

Table S9. Values of $\alpha$ and $\tau$ parameters obtained from generalized Debye model fitting of the $\tau(\nu)$ dependences for 2 at 500 Oe in the 1.8-3.4 K temperature range depicted in Figure S6b (columns 1-5) and at 2000 Oe in the 1.8-3.6 K temperature range depicted in Figure S6c (columns 6-10).

| $H$ (Oe) | $\alpha$ | sd | $\tau$ (s) | sd | $\alpha_2$ | sd | $\tau_2$ (s) | sd |
|----------|----------|----|------------|----|------------|----|------------|----|
| 1200     | 0.1273   | 0.0084 | 0.03223    | 0.00059 | 0.291      | 0.010 | 0.00256    | 0.00014 |
| 1400     | 0.1554   | 0.0053 | 0.03772    | 0.00038 | 0.270      | 0.008 | 0.00186    | 0.00006 |
| 1600     | 0.1358   | 0.0088 | 0.04542    | 0.00060 | 0.287      | 0.015 | 0.00156    | 0.00007 |
| 2000     | 0.1567   | 0.0084 | 0.05935    | 0.00065 | 0.298      | 0.020 | 0.000772   | 0.000026 |
| 3000     | 0.1883   | 0.0103 | 0.09998    | 0.00262 | 0.383      | 0.051 | 0.000115   | 0.000043 |
| 4000     | 0.2302   | 0.0046 | 0.16189    | 0.00342 | 0.369      | 0.038 | 0.000061   | 0.000028 |
| 5000     | 0.2488   | 0.0071 | 0.20793    | 0.00982 | 0.163      | 0.079 | 0.000237   | 0.000065 |

$T = 1.8$ K (Figure S6b)

| $H$ (Oe) | $\alpha$ | sd | $\tau$ (s) | sd | $\alpha_2$ | sd | $\tau_2$ (s) | sd |
|----------|----------|----|------------|----|------------|----|------------|----|
| 1.8      | 0.00507  | 0.000072 | 0.2739     | 0.0062 | 0.291      | 0.010 | 0.00256    | 0.00014 |
| 1.9      | 0.00393  | 0.000043 | 0.2469     | 0.0050 | 0.270      | 0.008 | 0.00186    | 0.00006 |
| 2.0      | 0.00314  | 0.000028 | 0.2223     | 0.0042 | 0.287      | 0.015 | 0.00156    | 0.00007 |
| 2.1      | 0.00254  | 0.000019 | 0.2002     | 0.0036 | 0.298      | 0.020 | 0.000772   | 0.000026 |
| 2.2      | 0.00203  | 0.000014 | 0.1784     | 0.0034 | 0.383      | 0.051 | 0.000115   | 0.000043 |
| 2.3      | 0.00162  | 0.000010 | 0.1584     | 0.0031 | 0.369      | 0.038 | 0.000061   | 0.000028 |
| 2.4      | 0.00129  | 0.000007 | 0.1406     | 0.0029 | 0.2045     | 0.0090 | 0.03608   | 0.00065 |
| 2.6      | 0.000817 | 0.0000046 | 0.1119    | 0.0029 | 0.2045     | 0.0090 | 0.03608   | 0.00065 |
| 2.8      | 0.0004968 | 0.0000032 | 0.0932    | 0.0029 | 0.2045     | 0.0090 | 0.03608   | 0.00065 |
| 3.0      | 0.0003085 | 0.0000030 | 0.0886    | 0.0035 | 0.2045     | 0.0090 | 0.03608   | 0.00065 |
| 3.2      | 0.0002003 | 0.0000034 | 0.0880    | 0.0048 | 0.2045     | 0.0090 | 0.03608   | 0.00065 |
| 3.4      | 0.0001443 | 0.0000045 | 0.0838    | 0.0069 | 0.2045     | 0.0090 | 0.03608   | 0.00065 |
| 3.6      | 0.0000385 | 0.0000050 | 0.0802    | 0.0083 | 0.2045     | 0.0090 | 0.03608   | 0.00065 |

$T = 1.8$ K (Figure S6c)

$H = 500$ Oe (Figure S6b)

$H = 2000$ Oe (Figure S6c)
Table S10. Values of the best-fit parameters obtained by fitting the $\tau^{-1}(H)$ using Eq. 1 (top part of the table) and the $\tau(T)$ using Eq. 2 (bottom part of the table) for compound 2. The relevant fits are shown as black lines in Figure 10b and 10d in the main text, respectively.

\[ \tau^{-1}(H) = \frac{A_1}{1+A_2H^2} + B_1H^4 + D \] \hspace{1cm} (Eq. 1)

\[ \ln(\tau^{-1}) = \ln[(A + B_2T + CT^n + \tau_0^{-2}\exp(-U_{eff}/k_BT))]^{-1} \] \hspace{1cm} (Eq. 2)

| Magnetic field dependence (black lines in Figure 10b) | branch 1 | branch 2 |
|------------------------------------------------------|----------|----------|
| $T$ (K)                                              | 1.8 K    | 1.8 K    |
| Frequency range (Hz)                                 | 1-1000   | 1-1000   |
| Field range (Oe)                                     | 200 – 5000 | 200 – 2000 |
| $A_1$ (s$^{-1}$)                                      | 967(98)  | 6585(51871) |
| $A_2$ (Oe$^{-2}$)                                     | 1.7(4) $10^{-5}$ | 0.0003(26) |
| $B_1$ (Oe$^{-4}$)                                     | 0 (fixed) | 7.9(6) $10^{-11}$ |
| $D$ (s$^{-1}$)                                        | 10(10)   | 107(45)  |
| $R^2$                                                 | 0.9876   | 0.9685   |

| Temperature dependence (black lines in Figure 10d)    |         |          |
|-------------------------------------------------------|----------|----------|
| $H_{DC}$ (Oe)                                         | 500      | 2000     |
| Frequency range (Hz)                                  | 1 – 1000 | 1 – 1000 |
| Temperature range (K)                                 | 1 – 3.4  | 1 – 3.6  |
| $A$ (s$^{-1}$)                                         | 0 (fixed) | 733(65)  |
| $B_2$ (s$^{-4}$K$^{-1}$Oe$^{-1}$)                      | 0 (fixed) |          |
| $C$ (s$^{-4}$K$^{-n}$)                                 | 6(1)     |          |
| $n$                                                   | 5.7(2)   |          |
| $R^2$                                                 | 0.9794   |          |
Figure S7. In-phase ($\chi'$) and out-of-phase ($\chi''$) AC susceptibilities for 2UV at 1.8 K measured in the 100-5000 Oe magnetic field range (a), at 500 Oe in the 1.8-3.4 K temperature range (b) and at 2000 Oe in the 1.8-3.6 K temperature range. Values of $\alpha$ and $\tau$ parameters are gathered in Table S11 (a) and S12 (b and c). The solid lines are the best fits to generalized Debye model.
Table S11. Values of $\alpha$ and $\tau$ parameters obtained from generalized Debye model fitting of the $\tau(\nu)$ dependences for 2UV at 1.8 K measured in the 100-5000 Oe magnetic field range depicted in Figure S7a.

| $H$ (Oe) | $\alpha$ | $sd$ | $\tau$ (s) | $sd$ |
|----------|----------|------|-----------|------|
| 100      | 0.1807   | 0.0104 | 0.00073   | 0.00002 |
| 200      | 0.2139   | 0.0077 | 0.00154   | 0.00003 |
| 300      | 0.2373   | 0.0076 | 0.00257   | 0.00004 |
| 400      | 0.2559   | 0.0074 | 0.00348   | 0.00006 |
| 500      | 0.2697   | 0.0068 | 0.00434   | 0.00007 |
| 600      | 0.2851   | 0.0067 | 0.00522   | 0.00008 |
| 700      | 0.3025   | 0.0069 | 0.00613   | 0.00010 |
| 800      | 0.3223   | 0.0074 | 0.00711   | 0.00013 |
| 1000     | 0.3637   | 0.0092 | 0.00944   | 0.00024 |

Table S12. Values of $\alpha$ and $\tau$ parameters obtained from generalized Debye model fitting of the $\tau(\nu)$ dependences for 2UV at 500 Oe in the 1.8-3.4 K temperature range depicted in Figure S7b (columns 1-5) and at 2000 Oe in the 1.8-4.0 K temperature range depicted in Figure S7c (columns 6-10), respectively.

| $T$ (K) | $\alpha$ | $sd$ | $\tau$ (s) | $sd$ | $\alpha$ | $sd$ | $\tau$ (s) | $sd$ |
|---------|----------|------|-----------|------|-----------|------|-----------|------|
| 1.8     | 0.00425  | 6.5E-05 | 0.2691   | 0.00082 | 1.8       | 0.1767  | 0.0023    | 0.04884 |
| 1.9     | 0.00337  | 4.3E-05 | 0.2445   | 0.00058 | 1.9       | 0.1909  | 0.0038    | 0.04189 |
| 2.0     | 0.00274  | 2.9E-05 | 0.2216   | 0.00050 | 2.0       | 0.2054  | 0.0027    | 0.03682 |
| 2.1     | 0.00224  | 2.2E-05 | 0.2001   | 0.00046 | 2.1       | 0.2075  | 0.0035    | 0.03342 |
| 2.2     | 0.00183  | 1.5E-05 | 0.1780   | 0.00040 | 2.2       | 0.2147  | 0.0063    | 0.03100 |
| 2.3     | 0.00148  | 1.1E-05 | 0.1587   | 0.00038 | 2.3       | 0.2299  | 0.0053    | 0.02890 |
| 2.4     | 0.00119  | 7.7E-06 | 0.1391   | 0.00033 | 2.4       | 0.2415  | 0.0059    | 0.02753 |
| 2.6     | 7.428E-04 | 4.7E-06 | 0.1073   | 0.00031 | 2.6       | 0.2811  | 0.0108    | 0.02631 |
| 2.8     | 4.632E-04 | 3.1E-06 | 0.0839   | 0.00030 | 2.8       | 0.2788  | 0.0158    | 0.02590 |
| 3.0     | 2.909E-04 | 2.9E-06 | 0.0725   | 0.00037 | 3.0       | 0.2952  | 0.0179    | 0.02797 |
| 3.2     | 1.875E-04 | 3.4E-06 | 0.0723   | 0.00050 | 3.2       | 0.3131  | 0.0295    | 0.03237 |
| 3.4     | 1.273E-04 | 4.4E-06 | 0.0715   | 0.00072 | 3.4       | 0.2398  | 0.0438    | 0.04095 |

| $H$ (Oe) | $\alpha$ | $sd$ | $\tau$ (s) | $sd$ | $\alpha$ | $sd$ | $\tau$ (s) | $sd$ |
|----------|----------|------|-----------|------|-----------|------|-----------|------|
| 100      | 0.1807   | 0.0104 | 0.00073   | 0.00002 |
| 200      | 0.2139   | 0.0077 | 0.00154   | 0.00003 |
| 300      | 0.2373   | 0.0076 | 0.00257   | 0.00004 |
| 400      | 0.2559   | 0.0074 | 0.00348   | 0.00006 |
| 500      | 0.2697   | 0.0068 | 0.00434   | 0.00007 |
| 600      | 0.2851   | 0.0067 | 0.00522   | 0.00008 |
| 700      | 0.3025   | 0.0069 | 0.00613   | 0.00010 |
| 800      | 0.3223   | 0.0074 | 0.00711   | 0.00013 |
| 1000     | 0.3637   | 0.0092 | 0.00944   | 0.00024 |
Table S13. Values of the best-fit parameters obtained by fitting the $\tau^{-1}(H)$ using Eq. 1 (top part of the table) and the $\tau(T)$ using Eq. 2 (bottom part of the table) for compound 2UV. The relevant fits are shown as blue lines in Figure 10b and 10d in the main text, respectively.

$\tau^{-1}(H) = A_1/(1+A_2H^2) + B_1H^4 + D$ \hspace{1cm} (Eq. 1)

$\ln\tau(T^{-1}) = \ln[(A + B_2 T + C T^n + D 0^{-1}\exp(-U_{eff}/k_B T))^{-1}]$ \hspace{1cm} (Eq. 2)

| Magnetic field dependence (blue lines in Figure 10b) | branch 1 | branch 2 |
|-----------------------------------------------------|----------|----------|
| $T$ (K)                                             | 1.8 K    | 1.8 K    |
| Frequency range (Hz)                                | 1-1000   | 1-1000   |
| Field range (Oe)                                    | 100 – 5000 | 100 – 2000 |
| $A_1$ (s$^{-1}$)                                     | 1966(134) | 2439(682) |
| $A_2$ (Oe$^{-2}$)                                    | 4.8(8)$\cdot$10$^{-5}$ | 9.7(53)$\cdot$10$^{-5}$ |
| $B_1$ (Oe$^{-4}$)                                    | 0        | 7.4(5)$\cdot$10$^{-11}$ |
| $D$ (s$^{-1}$)                                       | 36(14)   | 134(38)  |
| $R^2$                                               | 0.9897   | 0.9730   |

| Temperature dependence (blue lines in Figure 10d)   | H$_{DC}$ (Oe) | 500 | 2000 |
|-----------------------------------------------------|----------------|-----|------|
| Frequency range (Hz)                                | 1 – 1000       | 1 – 1000 |
| Temperature range (K)                               | 1 – 3.6        | 1 – 4.0|
| $A$ (s$^{-1}$)                                       | 0 (fixed)      | 750(78) |
| $B_2$ (s$^{-1}$K$^{-1}$Oe$^{-1}$)                    | 0 (fixed)      |       |
| $C$ (s$^{-1}$K$^{-n}$)                               | 7.4(14)        |      |
| $n$                                                  | 5.5(2)         |      |
| $R^2$                                               | 0.9731         |      |
Step-by-step preparation of 1,2-bis(2-methyl-5-pyridyl)thien-3-yl)perfluorocyclopentene (dtepy) according to a modified literature procedure\(^1\)

**Scheme 1.** Step-by-step preparation of 1,2-bis(2-methyl-5-pyridyl)thien-3-yl)perfluorocyclopentene (dtepy) starting from the commercially available 2-methylthiophene (A). Selected abbreviations: B = 3,5-dibromo-2-methylthiophene, C = (4-bromo-5-methylthiophen2-yl)boronic acid, D = 4-(4-bromo-5-methylthiophen-2-yl)pyridine, NBS = N-bromosuccinimide (Merck), B(OBu)\(_3\) = tributylborate (Merck), n-BuLi = 2.5 M n-butyllithium in hexanes (Merck).
Preparation of 3,5-dibromo-2-methylthiophene (B) according to the modified literature procedure

N-bromosuccinimide (9.05 g, 50.85 mmol, 2 eq) was dissolved in 60 ml of glacial acetic acid. Then the solution of 2-methylthiophene (2.46 ml, 25.42 mmol, 1 eq) in 25 ml of glacial acetic acid was added dropwise while stirring. The reaction mixture was stirred overnight at room temperature and then the content of the flask was poured into 400 ml of hexane and water mixture (1:1 by volume). The organic phase was separated and washed with 1 M NaOH and brine. The organic phase was dried over MgSO₄ and evaporated using rotavap. The obtained yellow oil was purified by vacuum distillation (90-110°C, 10 mbar) yielding 4.94 g of a colorless oil (76%). ¹H NMR (600 MHz, CDCl₃, Figure S8) δ 6.86 (s, 1H), 2.34 (s, 3H).

Figure S8. ¹H NMR spectrum of 3,5-dibromo-2-methylthiophene (B) recorded in CDCl₃ with TMS as the reference.
**Preparation of (4-bromo-5-methylthiophen2-yl)boronic acid (C)**

The following reaction was performed under inert gas atmosphere. 3,5-dibromo-2-methylthiophene (B) (9.7 g, 37.9 mmol, 1 eq) was dissolved in anhydrous THF in a two-necked round bottom flask. The mixture was cooled to -78 °C. To the stirred solution 2.5 M n-BuLi (16 ml, 39.8 mmol, 1.5 eq) was added dropwise. The reaction was stirred for 15 minutes at -78 °C and then tributyl borate (10.46 g, 45.5 mmol, 1.2 eq) was slowly added to the mixture followed by slow warm up to RT and further stirring at RT for 24h. The reaction mixture was quenched with 110 ml of 1M HCl and stirred for additional 1 h. Then THF was removed under vacuum and the mixture was extracted with Et₂O (3 × 50 ml). The organic layers were combined and the boronic acid was removed by washing with 2M NaOH solution (3 × 50 ml). The combined aqueous layers were carefully acidified to neutral using conc. HCl. The obtained off-white-to-yellow solid was filtered and dried under vacuum (yield: 5.5 g, 76%) and used without purification for the preparation of 4-(4-bromo-5-methylthiophen-2-yl)pyridine (D) as described in the next step described below. Crude ¹H NMR (300 MHz, DMSO; Figure S9) δ 8.28 (s, 2H), 7.50 (s, 1H), 2.37 (s, 3H).

![Figure S9. ¹H NMR spectrum of (4-bromo-5-methylthiophen2-yl)boronic acid (C) recorded in CDCl₃ with TMS as the reference.](image-url)
Preparation of 4-(4-bromo-5-methylthiophen-2-yl)pyridine (D)
The (4-bromo-5-methylthiophen2-yl)boronic acid (C) (4.0 g, 18.1 mmol, 1 eq), 4-iodopyridine (4.45 g, 21.7 mmol, 1.2 eq) and 50 ml THF were placed in a 200 ml Schlenk flask under inert atmosphere. Into the stirred solution under argon 50 ml of 20% Na$_2$CO$_3$ solution in degassed water was added and the reaction mixture was degassed again by performing three vacuum-inert gas cycles. Pd(PPh$_3$)$_4$ (1.04 g, 0.9 mmol, 5 mol%) was added and the reaction mixture was heated to 85 °C for 72 h under inert gas. After cooling to RT, the product was extracted from the mixture by two 50 ml portions of dichloromethane and the organic layers were washed with H$_2$O (2 × 50 ml) and brine (50 ml). After drying over MgSO$_4$ the solvent was removed under vacuum yielding an orange solid as the crude product. Purification by silica gel column chromatography (EtOAc) afforded a light yellow solid (4.32 g, 93% yield) as the final product. $^1$H NMR (300 MHz, CDCl$_3$; Figure S10) δ 8.58 (d, $J$ = 5.8 Hz, 2H), 7.36 (dd, $J$ = 4.6, 1.6 Hz, 2H), 7.30 (s, 1H), 2.44 (s, 3H).

![Figure S10](image_url). $^1$H NMR spectrum of 4-(4-bromo-5-methylthiophen-2-yl)pyridine (D) recorded in CDCl$_3$ with TMS as the reference.
Preparation of 1,2-bis(2'-methyl)-5'-({pyrid-4''-yl}thien-3'-yl)perfluorocyclopentene (dtepy)

4-(4-bromo-5-methylthiophen-2-yl)pyridine (D) (3.60 g, 14.2 mmol, 2 eq) was dissolved in 150 ml of anhydrous THF and 2.5 n-BuLi in hexanes (5.66 ml, 14.2 mmol, 2eq) was slowly added at -78 °C udner inert gas atmosphere. The solution turns deep red and perfluorocyclopentene (neat, 1.50 g, 7.1 mmol, 1 eq) was then slowly added using a cooled syringe. The green mixture is allowed to warm to RT and then stirred overnight. After that 40 ml of 1 M HCl was added and the reaction stirred for additional 30 min. THF was removed under vacuum and the residue was neutralized using saturated aqueous Na₂CO₃ followed by a few extractions using DCM (3 × 50 ml) and additional washings with saturated Na₂CO₃ (50 ml) and brine (50 ml). The product was purified by column chromatography over alumina (DCM/ACOEt = 4:1) yielding a greenish solid which becomes white after washing with pentane (0.50 g, 14%). ¹H NMR (300 MHz, CDCl₃, Figure S11) δ 8.62 (dd, J = 4.6, 1.5 Hz, 4H), 7.48 (s, 2H), 7.43 (dd, J = 4.6, 1.6 Hz, 4H), 2.01 (s, 6H).

Figure S11. ¹H NMR spectrum of 1,2-bis(2'-methyl)-5'-({pyrid-4''-yl}thien-3'-yl)perfluorocyclopentene (dtepy) recorded in CDCl₃ with TMS as the reference.
References in the Supporting Information:

1. Nikolayenko VI, Castell DC, van Heerden DP, Barbour LJ. Guest-Induced Structural Transformations in a Porous Halogen-Bonded Framework. *Angewandte Chemie International Edition* **57**, 12086-12091 (2018)

2. Valderrey V, Bonasera A, Fredrich S, Hecht S. Light-Activated Sensitive Probes for Amine Detection. *Angewandte Chemie International Edition* **56**, 1914-1918 (2017)