

*Towards Molecular Alloys: Computational and Experimental Studies on (p-NCC<sub>6</sub>F<sub>4</sub>CNSeSeN)<sub>x</sub>(p-NCC<sub>6</sub>F<sub>4</sub>CNSSN)<sub>1-x</sub>*

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### ESI-1 General Synthetic Methods

The preparation of **1** and **2** was undertaken under a nitrogen atmosphere using standard double-manifold techniques and dry solvents. Solids were stored and handled under a nitrogen atmosphere using an MBraun glovebox. Radicals **1** and **2** were both prepared according to literature methods.<sup>1,2</sup> Tetrafluoroterephthalonitrile and lithium bis(trimethylsilyl)amide (Sigma) were used as received. SCl<sub>2</sub> was prepared by chlorination of sulfur according to the literature method.<sup>3</sup>

IR spectra were recorded on a Bruker a-FT-IR spectrometer. Elemental analysis data were determined using a Perkin-Elmer 2400 elemental analyzer. For [**1**]Cl and [**2**]Cl data were fitted assuming LiCl as the contaminant but we recognize any non-organic impurity, such as S or Se, could equally lead to the low compositional CHN data. These contaminants in [**1**]Cl and [**2**]Cl were removed during the synthesis and purification of **1** and **2**. Single crystal X-ray diffraction data were recorded on a Bruker APEX III single crystal X-ray diffractometer equipped with a Mo- $\mu$ S microsource and Photon 100 detector. Cryogenic temperatures were maintained using an Oxford Instruments 700 series cryostream. The data collection strategy implemented the APEX-III software.<sup>4</sup> Data processing and reduction and an absorption correction employed Bruker SAINT and Bruker SADABS software respectively.<sup>5,6</sup> Structure solution utilized SHELXTL<sup>7</sup> and refinement was undertaken against  $F^2$  using SHELXTL.<sup>8</sup> Powder data were collected on a Bruker D8 Advance PXRD at room temperature using the DIFFRAC suite.<sup>9</sup> Baseline corrections were made within DASH.<sup>10</sup> EPR spectra were recorded in solution (CH<sub>2</sub>Cl<sub>2</sub>) or the solid state on a Bruker EMXplus X-band EPR running at ca 9.75 GHz at room temperature. EPR simulations implemented PIPPIN (M. Nilges, University of Illinois EPR Centre)<sup>11</sup> via the PIP4WIN EPR interface (J.M. Rawson, U. Windsor 2011).<sup>12</sup>

### ESI-2 Synthesis of **1**

- a) Synthesis of p-NCC<sub>6</sub>F<sub>4</sub>CNSSNCl ([**1**]Cl):** Tetrafluoroterephthalonitrile (2.00 g, 10.00 mmol) and lithium bis(trimethylsilyl) amide (1.673g, 10.00 mmol) were stirred together in Et<sub>2</sub>O (25 mL) for approximately 2 hours. Sulfur dichloride (1.48 mL, 22 mmol) was added dropwise at 0 °C affording an orange precipitate. The solvent was removed via cannula filtration and the solvent was washed with Et<sub>2</sub>O (3 × 25 mL). The solid was left to dry under a nitrogen atmosphere to yield the orange-yellow product, [**1**]Cl (2.753 g, 88%), contaminated with LiCl by-product. **IR:** 2254 (w, C≡N), 1633 (w, C=N), 534 (w, S-S), 1488 (m), 1433 (m), 1090 (w). **EA:** Calc. for (C<sub>8</sub>ClF<sub>4</sub>N<sub>3</sub>S<sub>2</sub>)(1.6 LiCl): C 25.18%, N 11.02%; Found C 25.20%, N 10.07%
- b) Synthesis of p-NCC<sub>6</sub>F<sub>4</sub>CNSSN• (**1**):** p-cyanotetrafluorophenyl dithiadiazolium chloride (1.50 g, 4.78 mmol) was reduced by heating with triphenyl antimony (0.84 g, 2.39 mmol) under a nitrogen atmosphere at 55 °C for ca. 1.5 hrs. The dark oil was then cooled and CH<sub>2</sub>Cl<sub>2</sub> (6 mL) was added. The reaction mixture was left to stir for 5 minutes. The solvent was removed *in vacuo* and a cold-finger added to the Schlenk tube against a nitrogen atmosphere. The dark product was slowly sublimed on the cold-finger under dynamic vacuum (110 – 20 °C) to yield **1 $\beta$**  (410 mg, 30 %) as black lustrous needles. **EPR** (X-band, 298 K, CH<sub>2</sub>Cl<sub>2</sub>)  $g = 2.015$ ,  $a_N = 5.13$  G; **IR:** 2250 (w, C≡N), 1630 (w, C=N), 1434 (m), 1329 (m), 1019 (m), 774 (s), 682 (s), 501 (w, S-S); **EA:** Calc. for C<sub>8</sub>F<sub>4</sub>N<sub>3</sub>S<sub>2</sub>: C 34.53%, N 15.10%; Found C 35.20% N 14.07%. PXRD studies confirmed phase purity as **1 $\beta$** .

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### ESI-3 Synthesis of **2**

- a) Synthesis of p-NCC<sub>6</sub>F<sub>4</sub>CNSeSeNCl [(2)Cl]:** Tetrafluoroterephthalonitrile (1.29 g, 6.45 mmol) and lithium bis(trimethylsilyl) amide (1.08g, 6.45 mmol) were stirred together in Et<sub>2</sub>O (20 mL) under a nitrogen atmosphere for approximately 2 hours. In a separate Schlenk, selenium tetrachloride (1.42 g, 6.45 mmol) and elemental selenium (0.509 g, 6.45 mmol) were stirred for approximately 2 hours as an *in situ* source of SeCl<sub>2</sub>. The selenium dichloride was added dropwise at 0 °C via cannula transfer, affording a brown precipitate. The solvent was removed via cannula filtration and the solvent was washed with Et<sub>2</sub>O (3 × 10) mL. To ensure complete removal of solvent, the solid was dried *in vacuo*. The solid was left to dry under a nitrogen atmosphere to yield the red product, *p*-cyanotetrafluorophenyl diselenadiazolium chloride (2.350 g, 90%). **IR:** 653 (s), 1059 (w), 1420 (m), 1484 (s), 1638 (w), 2251 (w, C≡N); **EA:** Calc. for C<sub>8</sub>ClF<sub>4</sub>N<sub>3</sub>Se<sub>2</sub> (2.5 LiCl) C: 19.50% N: 8.54%; Found C: 20.09% N: 8.53%.
- b) Synthesis of p-NCC<sub>6</sub>F<sub>4</sub>CNSeSeN·(2):** [(2)Cl], (0.774 g, 1.9 mmol) was reduced with molten triphenyl antimony (0.215 g, 0.61 mmol) under a nitrogen atmosphere at 55 °C for 1.5 hours. A water-cooled cold finger was added and the product was left to sublime under dynamic vacuum at 110 °C to yield **2** as a dark purple product on the cold-finger (90 mg, 13 %). **IR:** 685 (s), 731 (s), 1062 (m), 1435 (m), 1472 (m), 1688 (w, C=N), 2253 (w, C≡N). **EA:** Calc. for C<sub>8</sub>F<sub>4</sub>N<sub>3</sub>Se<sub>2</sub> C: 25.83% N: 11.30%; Found C: 26.52% N: 10.58%. **EPR** (X-band, 298 K): rhombic spectrum- g<sub>x</sub> = 2.004, g<sub>y</sub> = 2.016, g<sub>z</sub> = 2.107. PXRD studies confirmed purity of **2**.

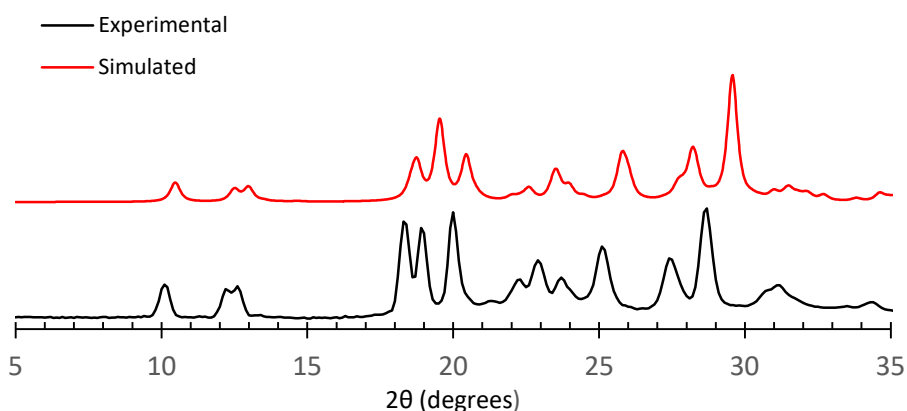
*Towards Molecular Alloys: Computational and Experimental Studies on (p-NCC<sub>6</sub>F<sub>4</sub>CNSeSeN)<sub>x</sub>(p-NCC<sub>6</sub>F<sub>4</sub>CNSSN)<sub>1-x</sub>*

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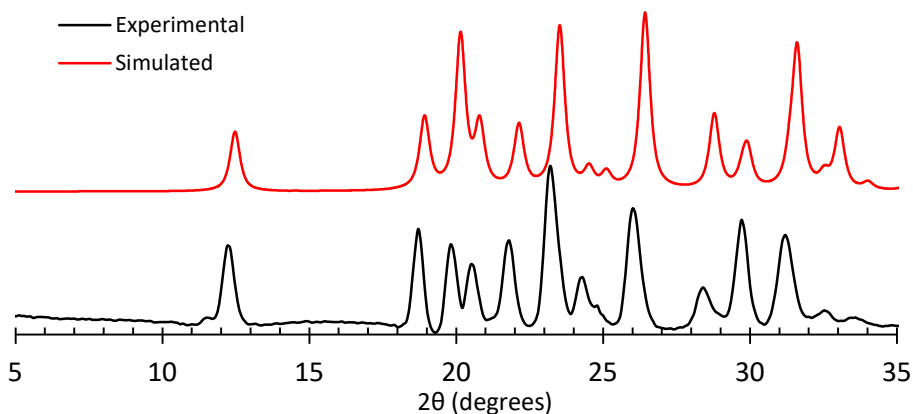
#### ESI-4: PXRD

PXRD measurements were made at ambient temperature on a Bruker D8 Discover using Cu-K $\alpha$  radiation equipped with a 0.5 mm collimator. Simulations of PXRD profiles for **1 $\alpha$** , **1 $\beta$**  and **2** were based on low temperature single crystal data. Small differences in peak positions are attributed to lattice expansion on warming. For alloys of **1** and **2**, PXRD profiles were simulated using a Rietveld refinement within Expo2014 using the LeBil method for non-structural parameters [A. Altomare, C. Cuocci, C. Giacovazzo, A. Moliterni, R. Rizzi, N. Corriero and A. Falcicchio, *J. Appl. Cryst.* 2013, *46*, 1231-1235].

**Figure S4.a) PXRD pattern of 1 $\alpha$  (from CH<sub>2</sub>Cl<sub>2</sub> solution)**



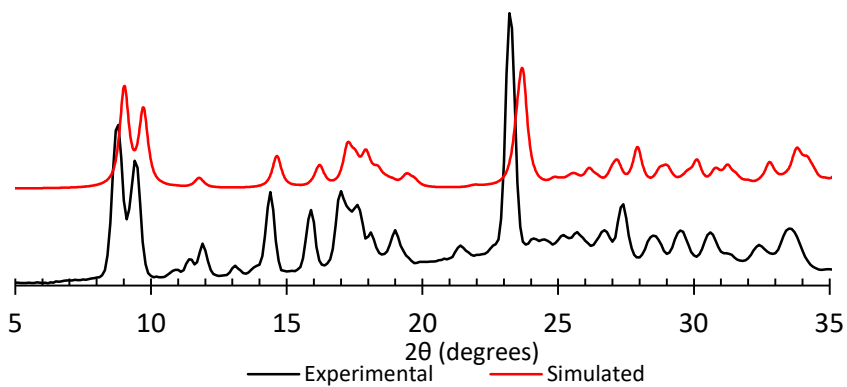
**Figure S4.b) PXRD pattern of 1 $\beta$  (prepared by sublimation)**



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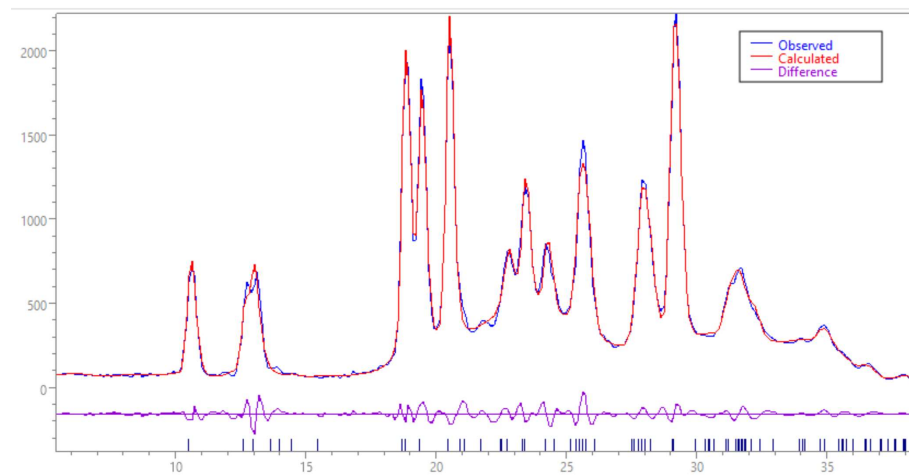
**Figure S4.c) PXRD pattern of 2 (prepared from CH<sub>2</sub>Cl<sub>2</sub> solution)**



**Figure S4.d) PXRD profile for 1α**

Rietveld refinement afforded:  $a = 7.6440$ ,  $b = 8.0002$ ,  $c = 9.566$  Å,  $\alpha = 65.715$ ,  $\beta = 68.006$ ,  $\gamma = 67.525^\circ$

$R_p = 4.371$ ,  $R_{wp} = 6.013$



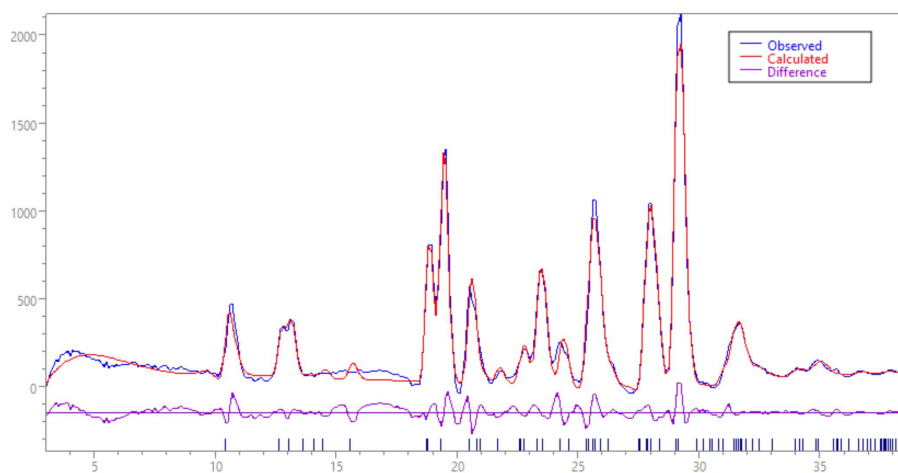
*Towards Molecular Alloys: Computational and Experimental Studies on (p-NCC<sub>6</sub>F<sub>4</sub>CNSeSeN)<sub>x</sub>(p-NCC<sub>6</sub>F<sub>4</sub>CNSSN)<sub>1-x</sub>*

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**Figure S4.e) PXR profile for 1<sub>0.95</sub>2<sub>0.05</sub>**

Rietveld refinement afforded:  $a = 7.5896$ ,  $b = 7.9552$ ,  $c = 9.6075$  Å,  $\alpha = 65.741$ ,  $\beta = 68.028$ ,  $\gamma = 67.782^\circ$

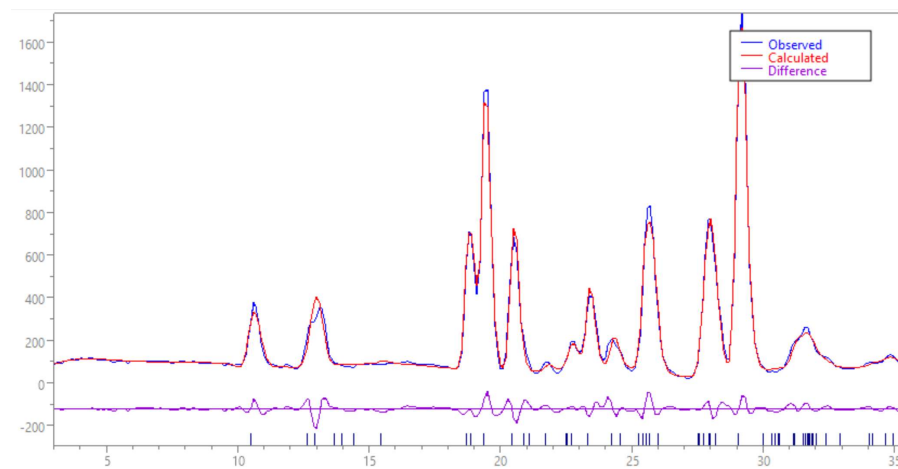
Rp = 12.362, Rwp = 19.148



**Figure S4.f) PXR profile for 1<sub>0.90</sub>2<sub>0.10</sub>**

Rietveld refinement afforded:  $a = 7.6656$ ,  $b = 7.9829$ ,  $c = 9.5696$  Å,  $\alpha = 65.572$ ,  $\beta = 67.944$ ,  $\gamma = 67.485^\circ$

Rp = 6.441, Rwp = 8.788



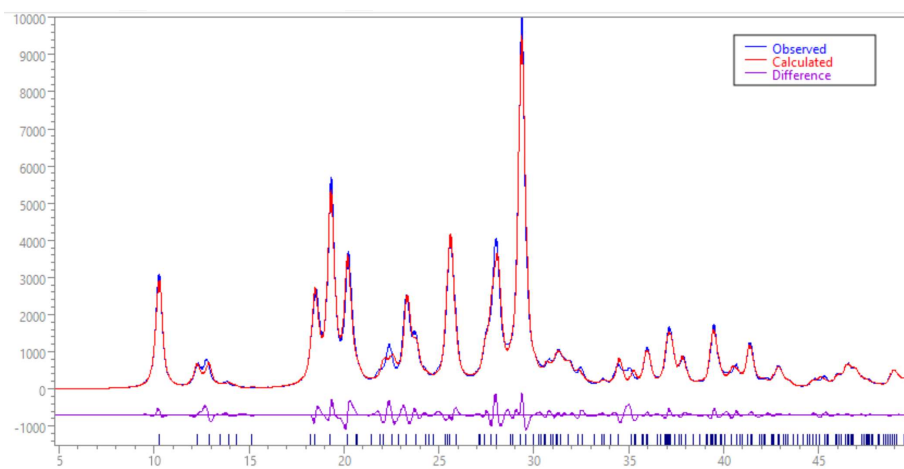
*Towards Molecular Alloys: Computational and Experimental Studies on (p-NCC<sub>6</sub>F<sub>4</sub>CNSeSeN)<sub>x</sub>(p-NCC<sub>6</sub>F<sub>4</sub>CNSSN)<sub>1-x</sub>*

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**Figure S4.g) PXRD profile for 1<sub>0.85</sub>2<sub>0.15</sub>**

Rietveld refinement afforded:  $a = 7.6731$ ,  $b = 8.1553$ ,  $c = 9.5661$  Å,  $\alpha = 66.876$ ,  $\beta = 68.633$ ,  $\gamma = 67.673^\circ$

$R_p = 7.006$ ,  $R_{wp} = 9.918$

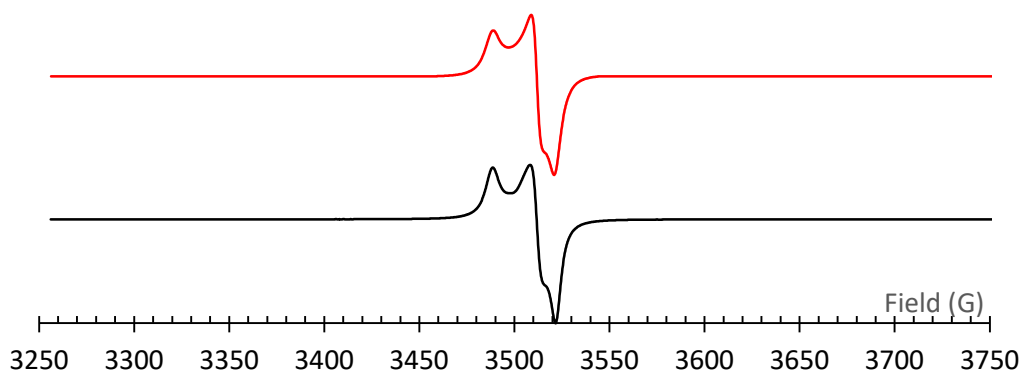


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**ESI-5 EPR of Starting Materials**

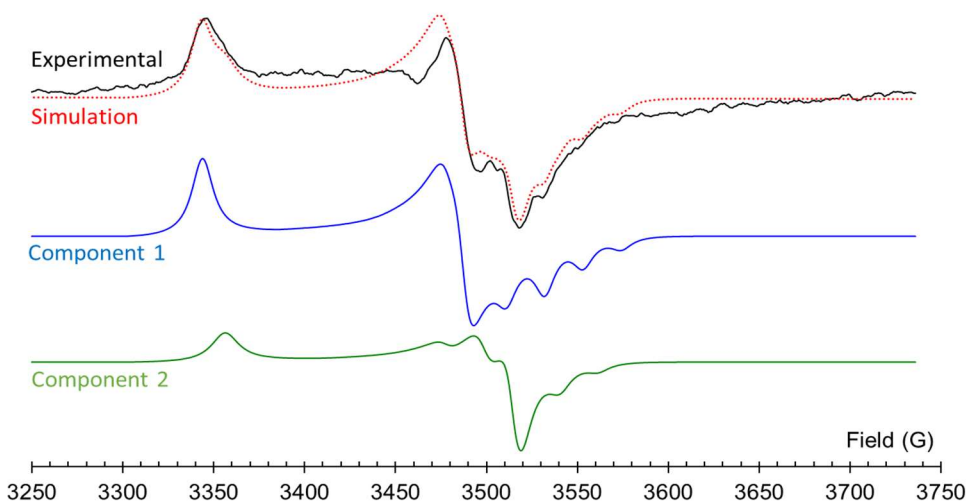
**ESI-5a: Solid state EPR spectrum of 1 $\alpha$**



**Figure S5.a) Solid state EPR of 1 $\alpha$ :** Simulation Parameters:  $g_x = 2.001$ ,  $g_y = 2.007$ ,  $g_z = 2.007$ ; Lorentzian linewidths:  $\Delta H(x) = 3.00$  G;  $\Delta H(y) = 3.25$  G;  $\Delta H(z) = 4.00$  G;  $S = 0.0093$ .

**ESI-5b: Solid state EPR spectrum of 2**

The EPR spectrum of solid **2** at room temperature could not be simulated using a single rhombic  $S = \frac{1}{2}$  spectrum but a composition of two chemically distinct  $S = \frac{1}{2}$  spectra in a 1:1 ratio. This is consistent with signals from the two chemically (crystallographically) independent  $S = \frac{1}{2}$  ions in a diamagnetic (**2**)<sub>2</sub> lattice. The simulation did not include low abundance <sup>77</sup>Se isotopomers.





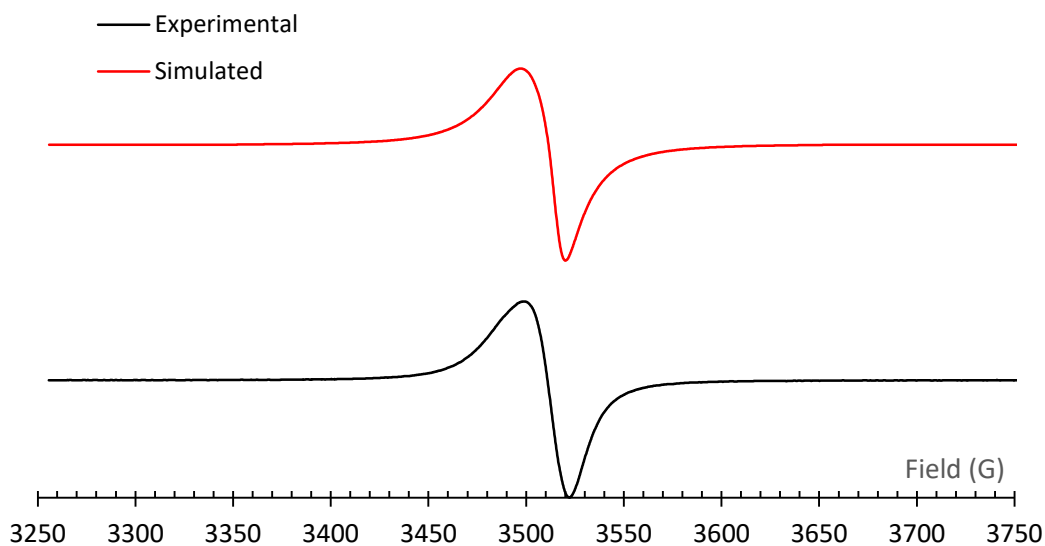
*Towards Molecular Alloys: Computational and Experimental Studies on (p-NCC<sub>6</sub>F<sub>4</sub>CNSeSeN)<sub>x</sub>(p-NCC<sub>6</sub>F<sub>4</sub>CNSSN)<sub>1-x</sub>*

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**Figure S5.b) 2 (solid state) Solid state EPR spectrum of 2:** Simulation Parameters: Component #1:  $g_x = 2.108$   $g_y = 2.021$   $g_z = 1.996$ ;  $a_{N(x)} = 0$ ,  $a_{N(y)} = 0$ ,  $a_{N(z)} = 21$  G;  $\Delta H_x = \Delta H_y = \Delta H_z = 7$  G<sub>pp</sub> (Lorentzian), weighting = 1. Component #2:  $g_x = 2.100$   $g_y = 2.006$   $g_z = 2.003$ ;  $a_{N(x)} = 0$ ,  $a_{N(y)} = 0$ ,  $a_{N(z)} = 21$  G,  $\Delta H_x = 9$ ,  $\Delta H_y = 6$ ,  $\Delta H_z = 8$  G<sub>pp</sub> (Lorentzian), weighting = 1.

**ESI-6 Solid State EPR Spectra of Alloys**

**ESI-6a: Solid state EPR spectrum of Alloy 1:2 = 95:5**

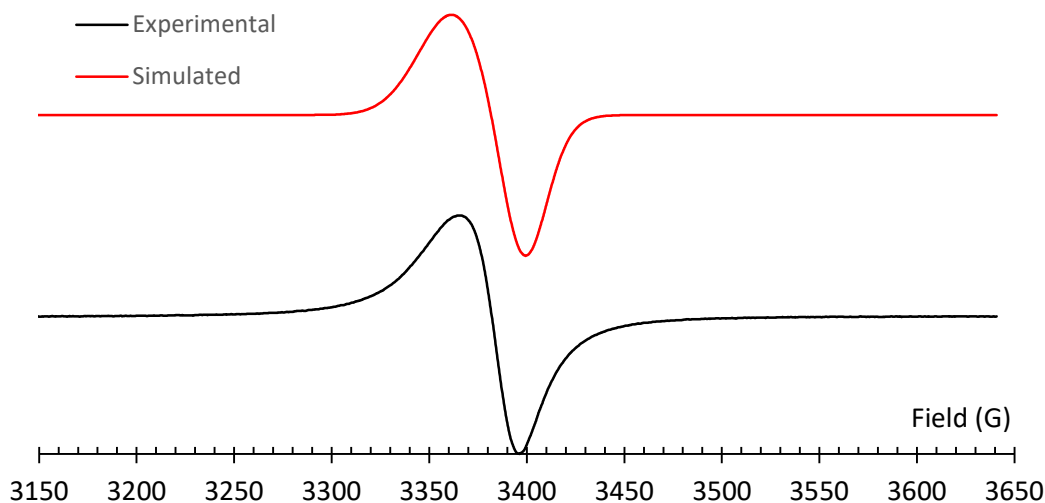


**Figure S6.a)** Solid state EPR spectrum of alloy  $1_{0.95}2_{0.05}$ . Simulation Parameters:  $g_x = 2.0047$ ,  $g_y = 2.012$ ,  $g_z = 2.012$ ; Lorentzian linewidths  $\Delta H_x = 7.00$  G,  $\Delta H_y = 25.25$  G,  $\Delta H_z = 25.25$  G.

**ESI-6b: Solid state EPR spectrum of Alloy 1:2 = 90:10**

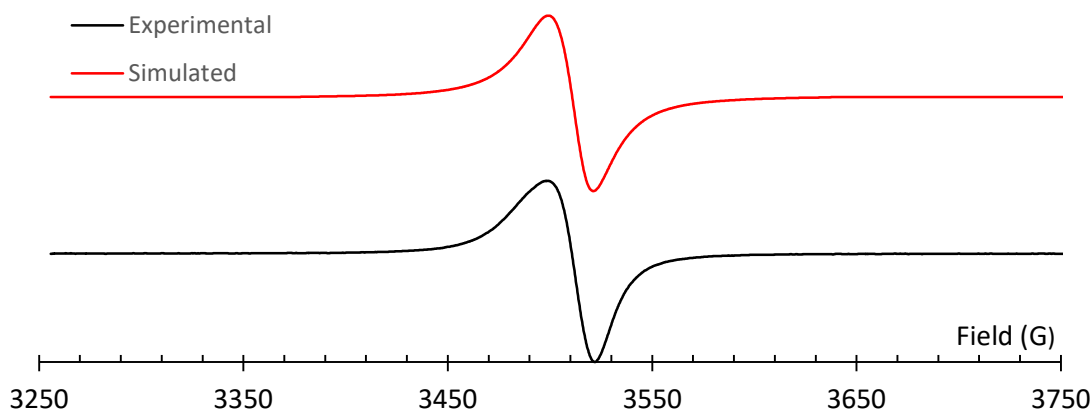
*Towards Molecular Alloys: Computational and Experimental Studies on (p-NCC<sub>6</sub>F<sub>4</sub>CNSeSeN)<sub>x</sub>(p-NCC<sub>6</sub>F<sub>4</sub>CNSSN)<sub>1-x</sub>*

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**Figure S6.b)** Solid state EPR spectrum of alloy  $1_{0.9}2_{0.1}$ . Simulation Parameters:  $g_x = 2.0149$ ,  $g_y = 2.0149$ ,  $g_z = 2.0005$ ; Gaussian linewidths  $\Delta H_x = 14$  G;  $\Delta H_y = 14$  G,  $\Delta H_z = 7.25$  G.

**ESI-6c: Solid state EPR spectrum of Alloy 1:2 = 85:15**



**Figure S6.c)** Solid state EPR spectrum of alloy  $1_{0.85}2_{0.15}$ . Simulation Parameters:  $g_x = 2.010$ ,  $g_y = 2.010$ ,  $g_z = 2.005$ ; Lorentzian linewidths  $\Delta H_x = 21.75$  G;  $\Delta H_y = 21.75$  G;  $\Delta H_z = 10.75$  G.

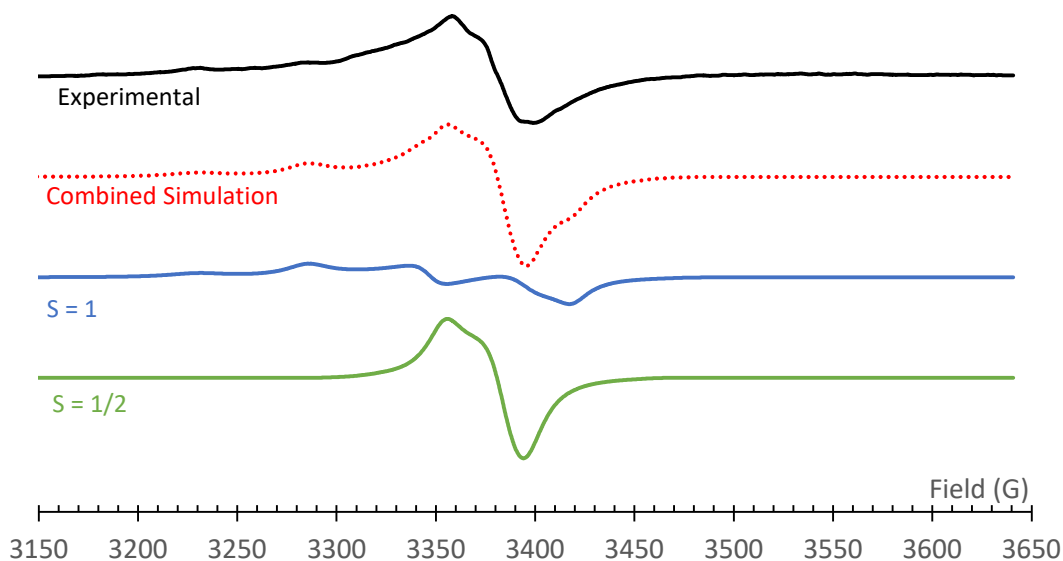
**ESI-6d: Solid state EPR spectrum of Alloy 1:2 = 80:20**

Initial simulation of this mixture used a single set of anisotropic g-tensors for an  $S = \frac{1}{2}$  radical system. However, this failed to replicate weak features evident to low field. These low intensity features were

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fitted using a thermally accessible excited  $S = 1$  system with small zero field splitting. Such features have been observed previously for DTDA dimers in the solid state.



**Figure S6.d)** Solid state EPR spectrum of alloy  $1_{0.80}2_{0.20}$ . Simulation Parameters: Component 1 ( $S = \frac{1}{2}$ ):  $g_x = 2.000$ ,  $g_y = 2.007$ ,  $g_z = 2.024$ ;  $\Delta H_x = 12$  G,  $\Delta H_y = 12$  G;  $\Delta H_z = 11$  G; weighting: 0.12. Component 2 ( $S=1$ ):  $g_x = 2.007$ ,  $g_y = 2.033$ ,  $g_z = 2.046$ ;  $\Delta H_x = 10$  G;  $\Delta H_y = 13$  G;  $\Delta H_z = 19$  G,  $|D| = 0.0085$ ,  $|E| = 0.0006$  cm<sup>-1</sup>