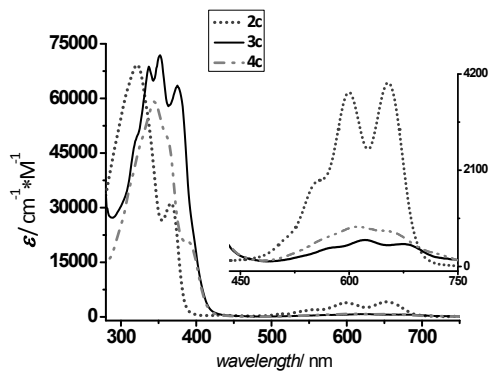
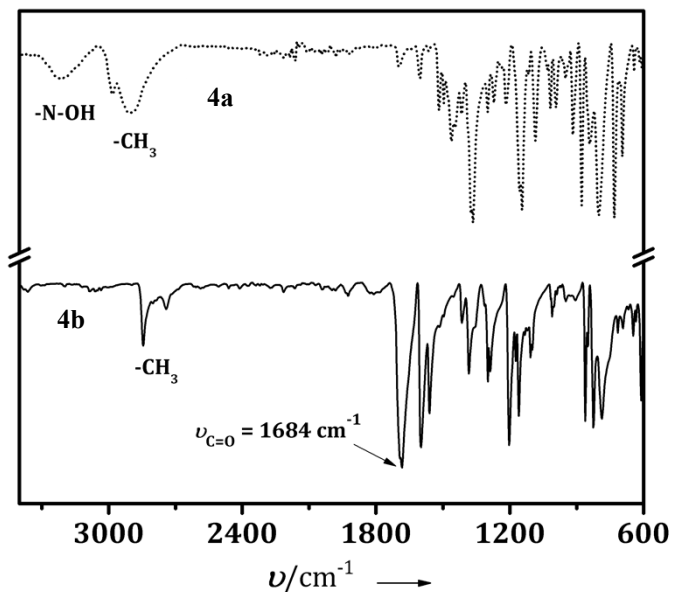


**Electronic Supplementary Information (ESI) available:** [Interacting Networks of Purely Organic Spin- $\frac{1}{2}$  Dimers]. See DOI:

1) **Optical absorption spectra**



**Figure S1** UV-Vis spectra of the nitronyl nitroxide radicals **2c-4c** recorded in toluene solutions at room temperature.



**Figure S2** Comparison of the FT-IR spectra of the starting dialdehyde **4a** with the corresponding condensation product **4b**.

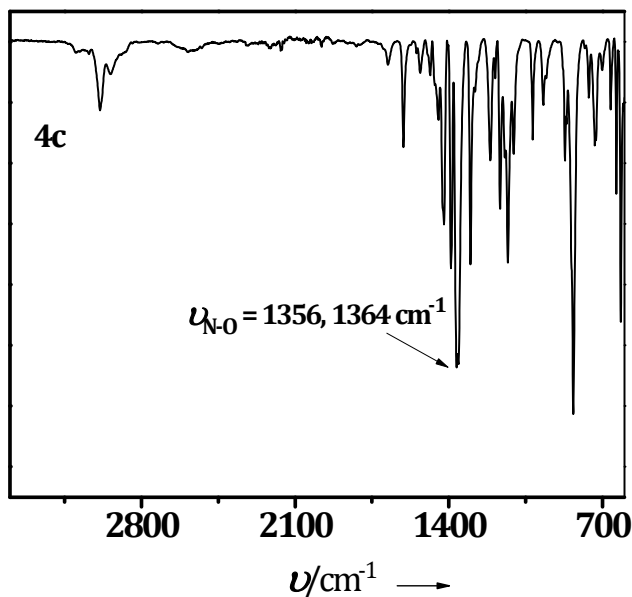


Figure S3 FT-IR spectra of the nitronyl nitroxide biradical **4c**.

## 2) EPR spectroscopy

EPR spectra of the studied biradicals **1c-4c** (black lines, Observed) recorded in diluted ( $10^{-4}$  M) and oxygen-free toluene solutions at  $T = 298$  K. Typical experimental parameters: 9.4 GHz frequency, 100 kHz modulation frequency, 5 mW microwave power, 0.012 mT modulation amplitude. The red lines (Simulated) show the computer simulated EPR spectra obtained by matrix diagonalization of the spin-Hamiltonian ( $\hat{H}$ ),  $\hat{H} = g\beta B_0 \hat{S}_{a,b} - 2J\hat{S}_a\hat{S}_b + \sum_{ij} aN_{ij} \times (\hat{S}_a\hat{N}_{ij} + \hat{S}_b\hat{N}_{ij})$ , with exchange-term  $|J| \geq 80$  mT, and suitable  $a_N$  (see Table 1 in the article), line-width tensor  $L_{x,y,z}$  of 0.1, 0.1, 0.1 mT.

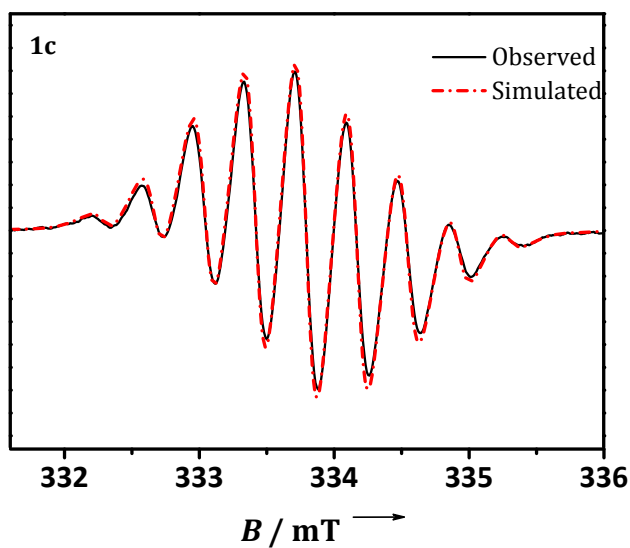


Figure S4 EPR spectrum of the nitronyl biradical **1c**.

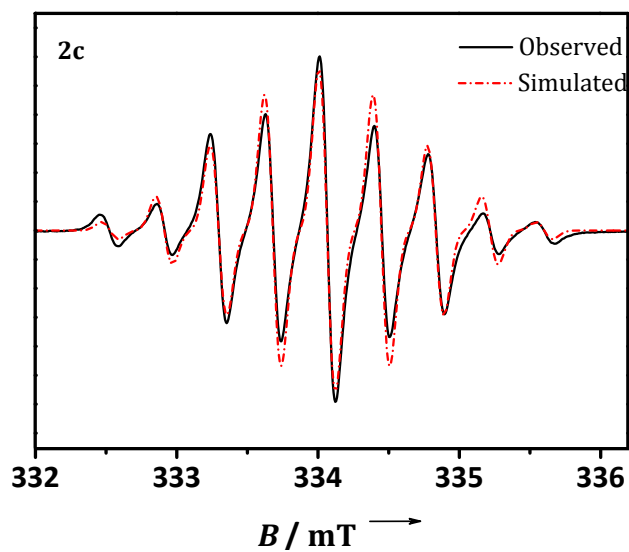


Figure S5 EPR spectrum of the nitronyl biradical 2c.

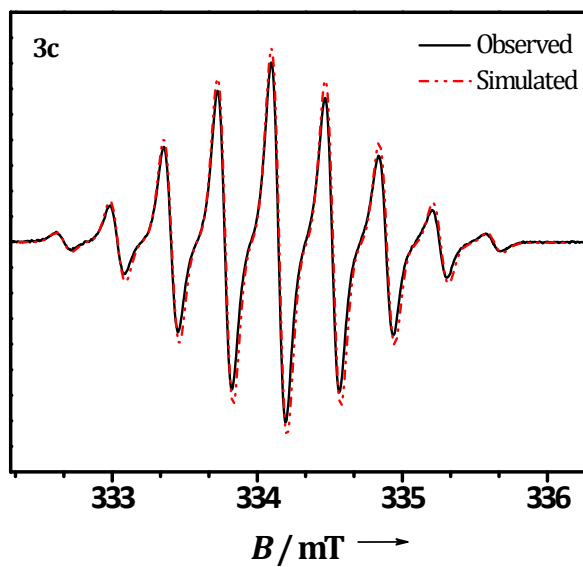


Figure S6 EPR spectrum of the nitronyl biradical 3c.

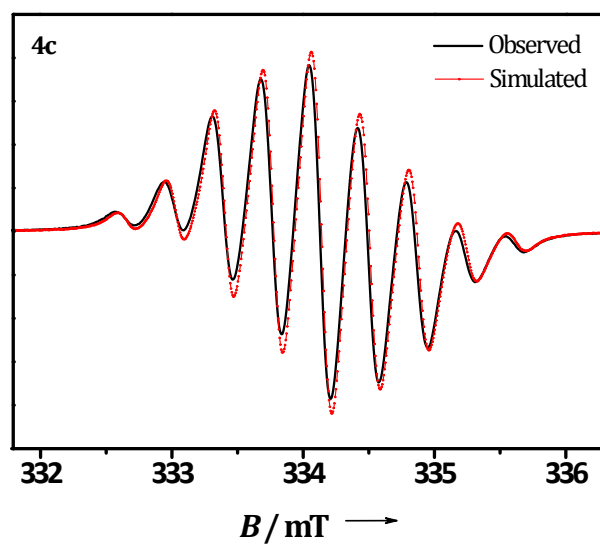


Figure S7 EPR spectrum of the nitronyl biradical **4c**.

### 3) Magnetic susceptibility

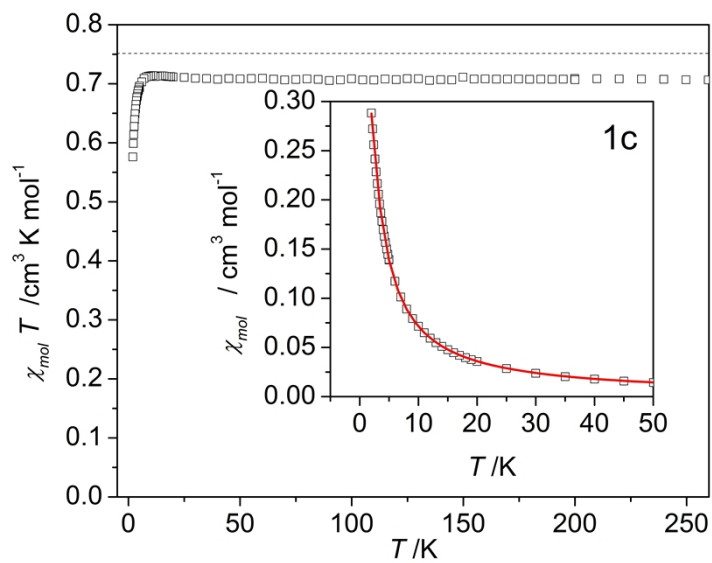
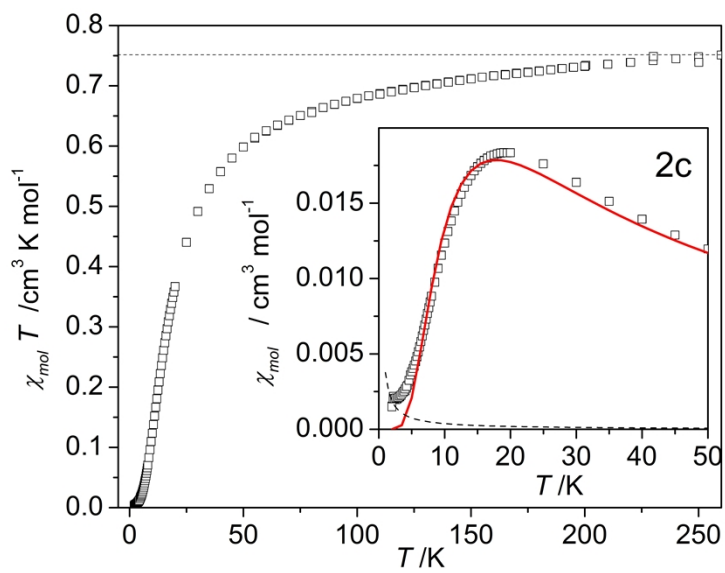
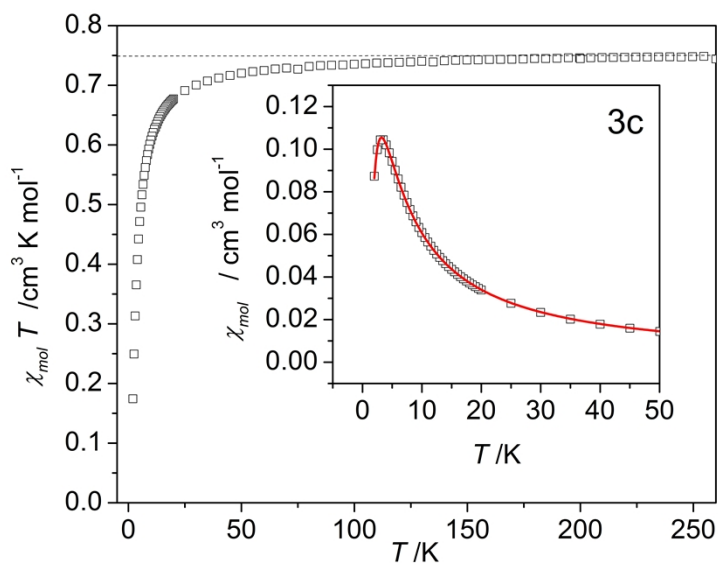


Figure S8 Effective magnetic moment  $\mu_{\text{eff}} = \chi \cdot T$  per spin  $S = \frac{1}{2}$  of biradical **1c**.



**Figure S9** Effective magnetic moment  $\mu_{\text{eff}} = \chi \cdot T$  per spin  $S = \frac{1}{2}$  of biradical **2c**.



**Figure S10** Effective magnetic moment  $\mu_{\text{eff}} = \chi \cdot T$  per spin  $S = \frac{1}{2}$  of biradical **3c**.

#### 4) Crystal structure and TOC graphic

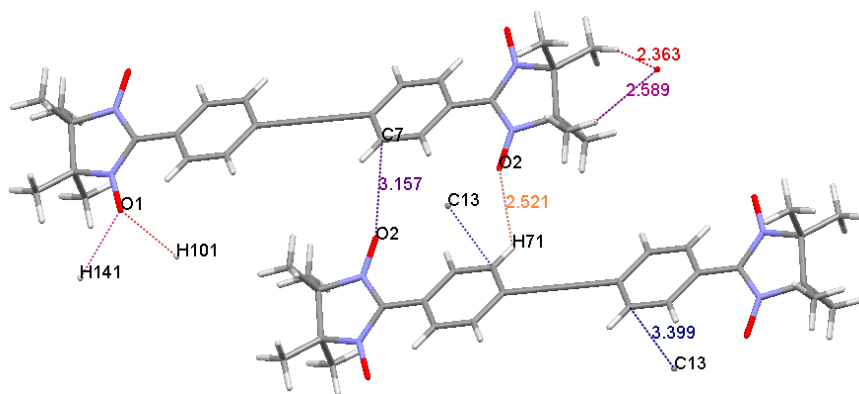


Figure S11 Fragment of the crystal packing of **4c** with emphasized short contacts.

The fine-tuning of the *intramolecular* exchange interactions in  $\pi$ -conjugated nitronyl nitroxide biradicals and their crystalline network formation is described.

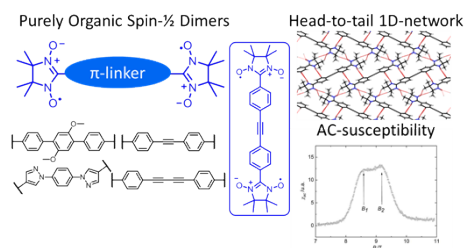


Figure TOC graphic