Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information for

Spin-Dimer Networks: Engineering Tools to Adjust the Magnetic Interactions in Biradicals

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Table S1. Selected structural data for the nitronyl **1c**, **2c** and imino **1d**, **3d**, **4d**, **5d** nitroxide biradicals

	1c	**2c**	**1d**	**3d**	**4d**	**5d**
Formula	$C_{26}H_{30}N_6O_4$	$C_{26}H_{30}N_6O_4$	$C_{26}H_{30}N_6O_2$	$C_{26}H_{32}N_4O_2$	$C_{24}H_{30}N_6O_2$	$C_{28}H_{32}N_4O_2$
M	490	490	458	432	434	456
crystal system	triclinic	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
space group	*P-1*	$P2_1/c$	*P-1*	$P2_1/n$	$P2_1/n$	$P2_1/n$
a, Å	7.3674(2)	10.0305(5)	7.0420(3)	6.2359(6)	6.3011(2)	6.6883(2)
b, Å	13.0178(4)	10.5040(7)	12.9582(9)	10.5265(7)	10.4759(5)	10.3043(4)
c, Å	13.7189(4)	12.3508(6)	14.2234(9)	17.6917(9)	17.1953(7)	18.2359(5)
α, deg	90.9445(14)	90	94.407(3)	90	90	90
β, deg	104.498(2)	102.582(3)	103.761(2)	94.553(4)	98.045	93.231(2)
γ, deg	104.2092(16)	90	102.863(3)	90	90	90
V, A^3	1230.61	1270.04	1217.41	1157.66	1123.89(8)	1254.79(7)
Z	2	2	2	2	2	2
R_{factor}(%)	5.24	5.5	6.21	5.18	5.26	4.01
D_c, $g \times cm^{-3}$	1.324	1.283	1.251	1.241	1.284	1.208
N_{ref}	7176	3696	6769	2527	3217	3669
N_{par}	325	163	334	154	154	154
S	0.986	1.073	0.978	1.025	1.091	1.112
CCDC	823716	816632	816630	823717	858078	810139

The crystallographic data were collected on Nonius Kappa CCD (Mo kα, μ = 0.71073 Å) diffractometer equipped with a graphite monochromator

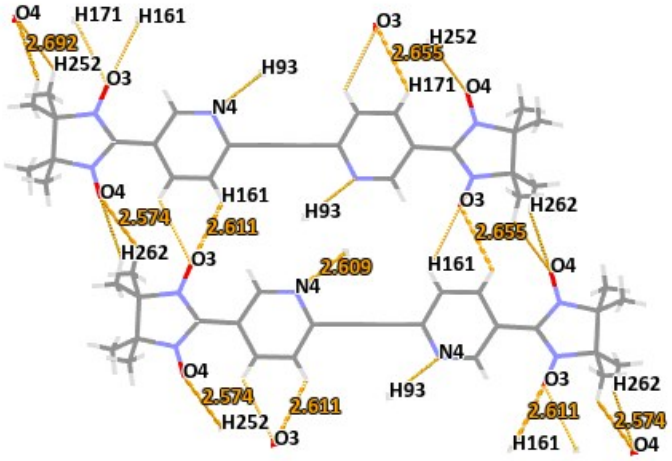

Figure S1. Fragment of the dimeric couple in crystal packing of **1c** with the emphasized short contacts.

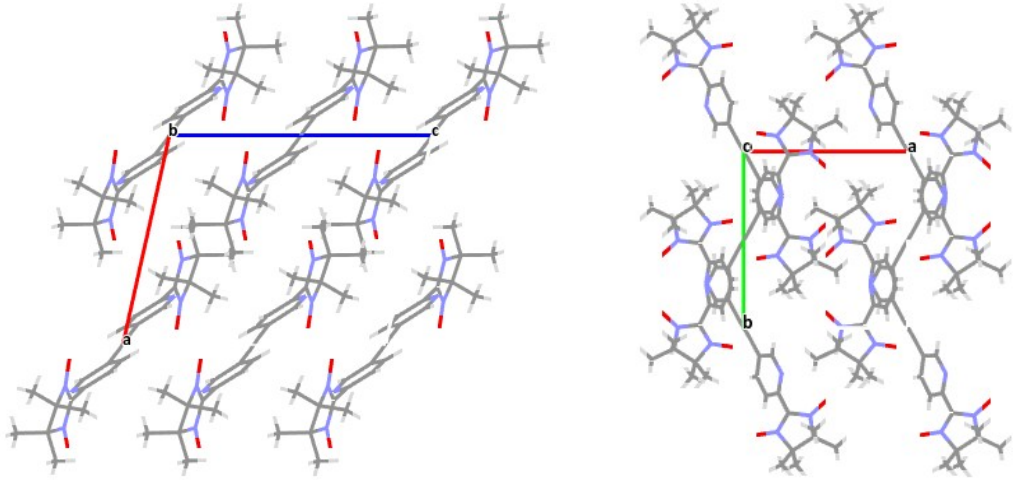

Figure S2. Crystal packing of biradical **2c**: view along the b axes (left) and c axes (right).

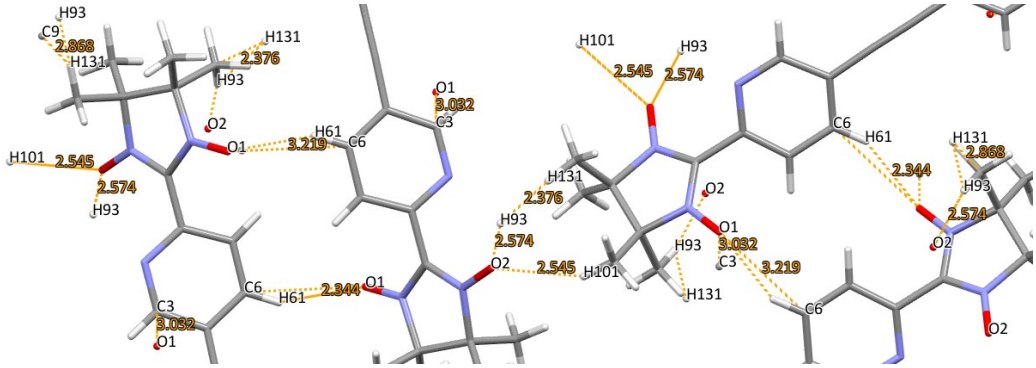

Figure S3. Fragment of the crystal packing of **2c** with emphasized short contacts and π-stacking**.**

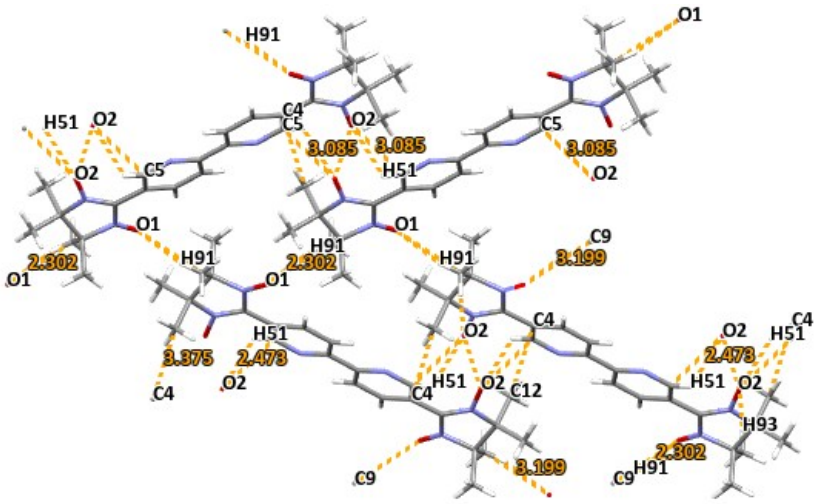

Figure S4. Fragment of the crystal packing of **4d** with emphasized short contacts and π-stacking (view along the *a* axes).

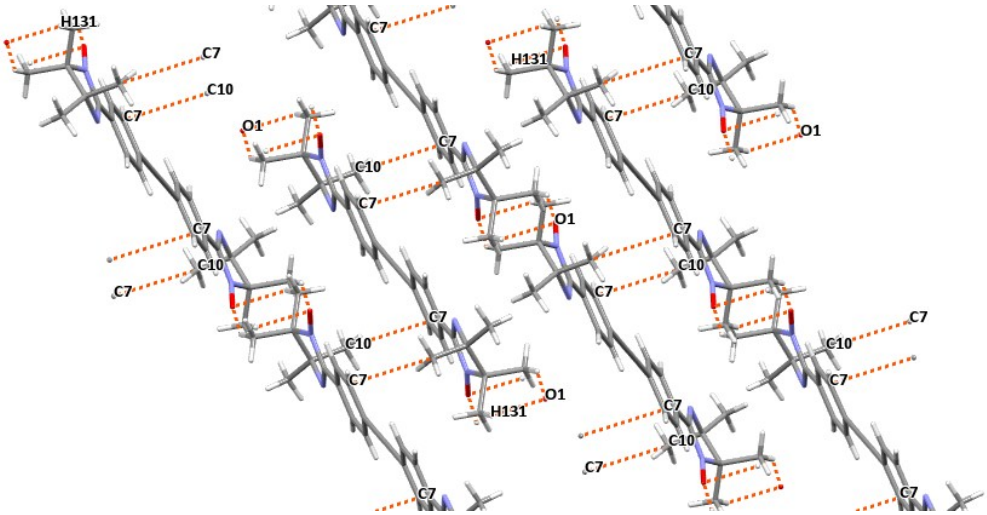

Figure S5. Fragments of the crystal packing of **5d** viewed along the *b* axes.

Table S2 Selected spectroscopic data for the nitroxide biradicals **1c**, **2c**, **1d**, **3d**, **4d**, **5d**

Biradical	IR[a] ν_{NO}/cm^{-1}	UV-Vis[b] λ_{max}/nm (ε/M^{-1}cm^{-1})[b]	Mass[c] g/mol	EPR a_N/mT
1c	1348	627 (557)	489	0.738
2c	1360	589 (502)	489	0.752
1d	1368	467 (944)	457	0.430, 0.885
3d	1364	461 (1090)	431	0.430, 0.870
4d	1366	462 (1021)	433	0.430, 0.849
5d	1365	468 (1091)	455	0.430, 0.849

[a] Measured in solid state at room temperature (*T* = 293 K);

[b] Measured in toluene solution;

[c] Measured in dichloromethane by FAB. The m/z$^+$ (100%) peak corresponds to [M]$^+$

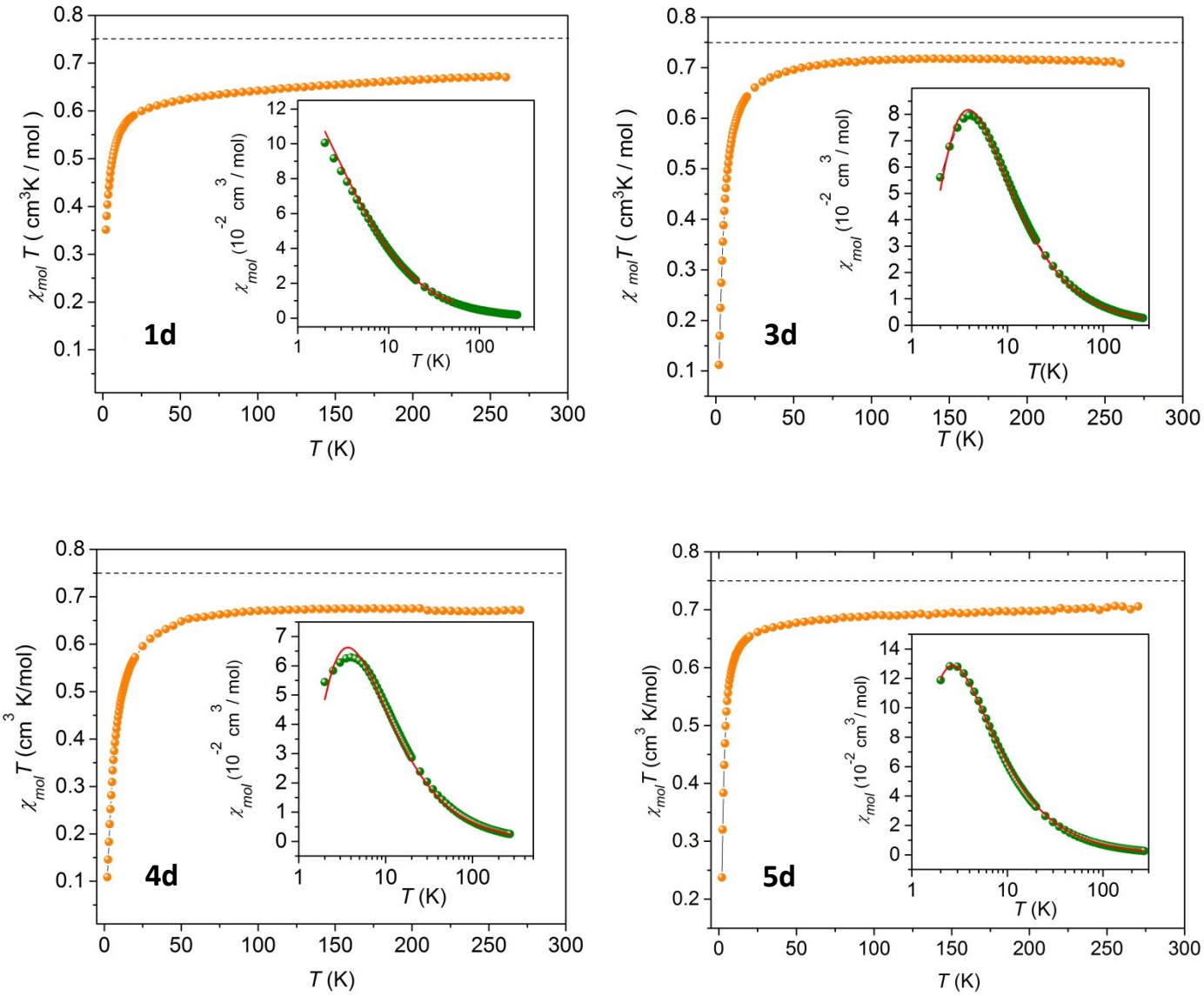

Figure S6. Effective magnetic moment $\mu_{\text{eff}} = \chi \cdot T$ per S = ½ spin of biradicals **1d**, **3d**, **4d** and **5d**. Inset: molar susceptibility χ_{mol} as a function of temperature together with fitting calculation.

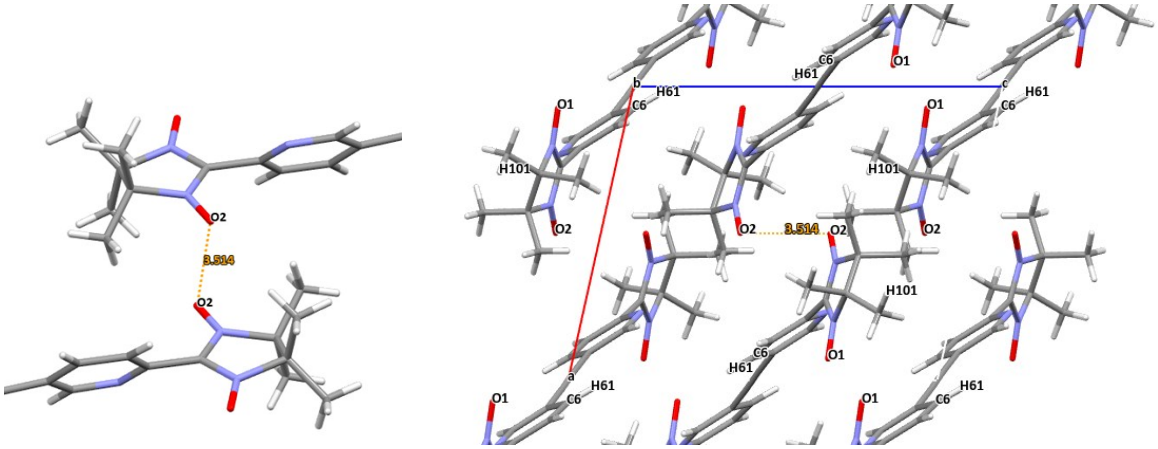

Figure S7. Crystal structure of the nitronyl biradical **2c**: fragment of the structure with emphasized short antiferromagnetic contacts of 3.514 Å, where the second radical unit of each biradical was replaced by H for the calculations.