Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary information

3D Molecular Network and Magnetic Ordering, Formed by Multi-Dentate Magnetic Couplers of Bis(benzene)chromium(I) and [1,2,5]Thiadiazolo [3,4-*c*][1,2,5]thiadiazolidyl

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Table S1 Selected bond lengths for TDTD, $Cr(C_6H_6)_2$ and $[Cr(C_6H_6)_2][TDTD]$.

Selected bond lengths for TDTD / Å		
	TDTD[a]	$[Cr(C_6H_6)_2][TDTD]$[b]
S-N	1.619(2) 1.619(2)	1.6587(16) 1.6661(19)
N-C	1.351(3) 1.348(3)	1.341(2) 1.343(2)
C-C	1.429(4)	1.449(3)

Selected bond lengths for $Cr(C_6H_6)_2$ / Å		
	$Cr(C_6H_6)_2$[c]	$[Cr(C_6H_6)_2][TDTD]$[b]
Cr-C	2.143(2) 2.140(2)	2.1515(19) 2.1517(18) 2.1336(18) 2.1418(18) 2.1528(18) 2.154(2)
C-C	1.417(3) 1.416(3)	1.420(3) 1.413(2) 1.418(2) 1.414(3) 1.419(2) 1.412(2)

[a] Ref 12. [b] This work. [c] Ref 15.

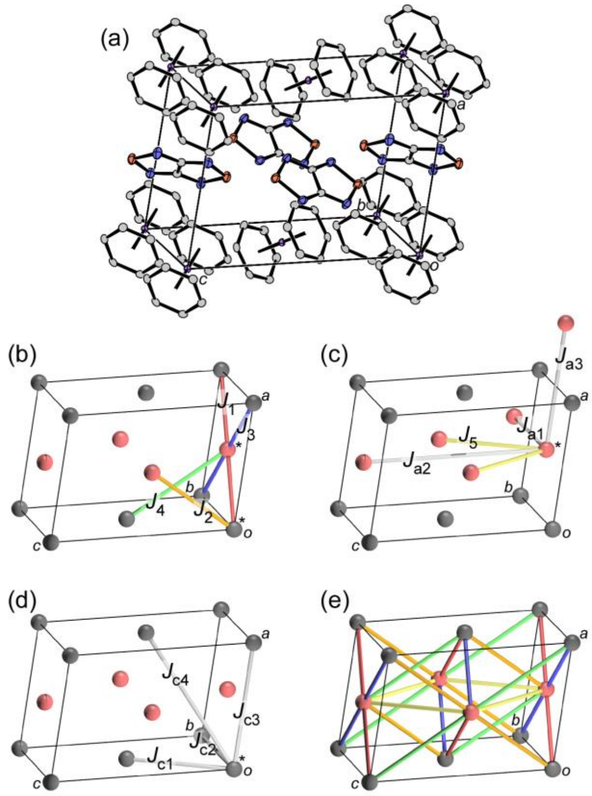

Fig. S1 Molecular packing (a) and its magnetic interactions *J* (b-e): Magnetic interactions between $[Cr(C_6H_6)_2]^+$ and $[TDTD]^-$ (b), $[TDTD]^-$ and $[TDTD]^-$ (c), and $[Cr(C_6H_6)_2]^+$ and $[Cr(C_6H_6)_2]^+$ (d) around asterisked molecules. Effective magnetic interactions in a unit cell (e). Gray and red spheres indicates the positions of $[Cr(C_6H_6)_2]^+$ and $[TDTD]^-$. Red, orange, blue, green, yellow and gray lines indicate the representative magnetic interactions J_1, J_2, J_3, J_4 and J_5, and negligibly small interactions, respectively. Calculated *J* values are listed in Table S2.

Table S2 Intermolecular magnetic coupling constants J in the crystal structure of $[Cr(C_6H_6)][TDTD]$ calculated by DFT, CASSCF and NEVPT2 procedures.

	Chain	Directions	J / cm^{-1}		
			DFT	CASSCF	NEVPT2
$[Cr(C_6H_6)_2]^+ \cdots [TDTD]^-$					
J_1 (red)	C	[110], $[1\bar{1}0]$		−3.60[c]	−8.96[e]
J_2 (orange)	B	[101]		1.68[c]	1.70[e]
J_3 (blue)	A	[110], $[1\bar{1}0]$		0.06[c]	−0.30[e]
J_4 (green)		$[10\bar{1}]$		0.59[c]	−1.44[e]
$[TDTD]^- \cdots [TDTD]^-$					
J_5 (yellow)		[011], $[01\bar{1}]$	−3.09[a]	0.29[d]	−1.16[e]
J_{a1}		[010]	0.00[a]		
J_{a2}		[001]	0.00[a]		
J_{a3}		[100]	0.00[a]		
$[Cr(C_6H_6)_2]^+ \cdots [Cr(C_6H_6)_2]^+$					
J_{c1}		[011]	−0.05[b]		
J_{c2}		[010]	−0.07[b]		
J_{c3}		[100]	0.11[b]		
J_{c4}		[211]	0.02[b]		

Level of theory and basis sets:

[a]BS-UB3LYP/TZVP, [b]FS-B3LYP/TZVP, [c]SA-CASSCF(16,13)/TZVP, [d]SA-CASSCF(14,14)/TZVP, [e] SA-CASSCF(14,14)/NEVPT2/TZVP

The exchange interactions for pairs $[Cr(C_6H_6)_2]^+ \cdots [TDTD]^-$ predicted using the BS-DFT approach were unreasonably strong (thousands of cm^{-1}). This effect is due to the incorrect wavefunction of the BS-singlet state of these pairs corresponding to the significant back charge transfer from $[TDTD]^-$ to $[Cr(C_6H_6)_2]^+$.