

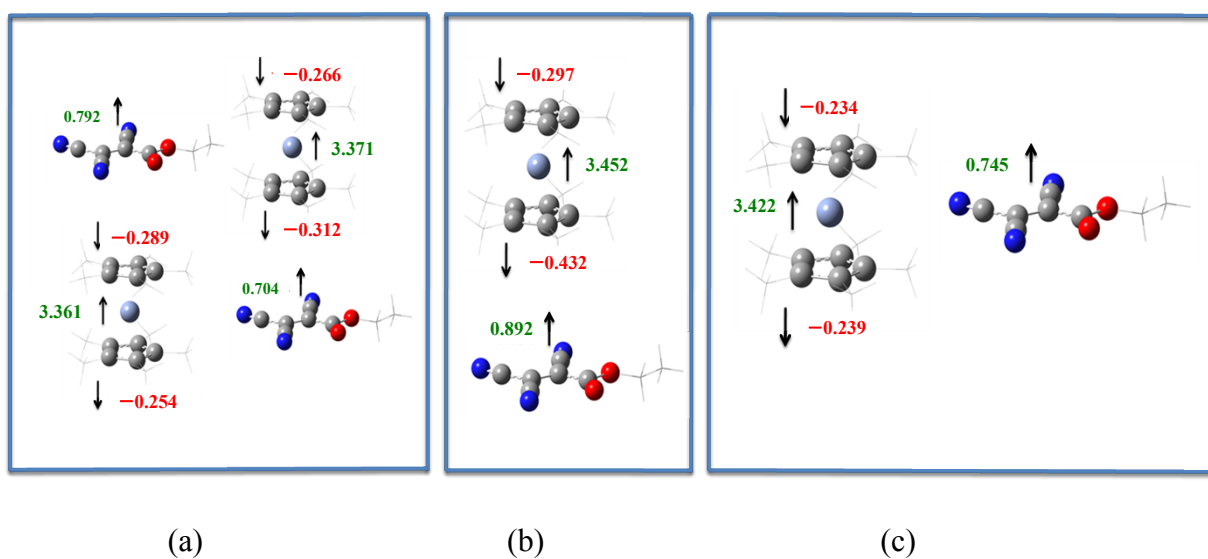
## Electronic Supplementary Information

### Effect of Charge Transfer and Periodicity on the Magnetism of [Cr(Cp\*)<sub>2</sub>][ETCE]

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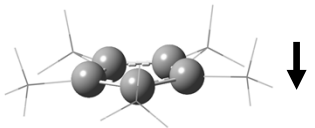

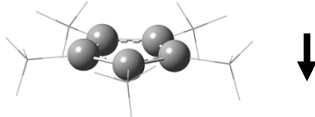



**Fig. S1** Spin populations of the high spin states plotted in (a) two dimensional array (b) V-pair and (c) H-pair of the donor-acceptor complex.

**Table S1** Energy comparison of triplet and quintet spin states in neutral  $[\text{Cr}^{\text{II}}(\text{Cp}^*)_2]$ 

Level of Theory	Energy difference between the quintet and triplet state in a.u.
UBHandHLYP/6-311++G(d,p) with LANL2DZ as extrabasis on Cr	0.005
CASSCF(6,8)/LANL2DZ	0.003
UBPW91/6-311++G(d,p) with LANL2DZ as extrabasis on Cr	0.042
UB3LYP/6-311++G(d,p) with LANL2DZ as extrabasis on Cr	0.028

**Table S2** Spin populations at the vertical donor-acceptor stack in different functionals (percentage of HF exchange are given for each functional in the parenthesis)

Functionals	UBHandHLYP	UBPW91	UB3LYP	UPBEPBE	UTPSSH
<b>% of Hartree-Fock Exchange</b>	<b>50<sup>t1</sup></b>	<b>0<sup>t2</sup></b>	<b>20<sup>t1</sup></b>	<b>0<sup>t1</sup></b>	<b>10<sup>46</sup></b>
	-0.297	-0.250	-0.249	-0.255	-0.228
	3.452	3.498	3.423	3.482	3.465
	-0.432	-0.385	-0.373	-0.358	-0.381
	0.892	0.727	0.790	0.706	-0.829
<b>Magnetic exchange coupling constants (J) in cm<sup>-1</sup></b>	<b>511</b>	<b>142</b>	<b>137</b>	<b>133</b>	<b>408</b>

t1 A. Sorkin, M. A. Iron and D. G. Truhlar, *J. Chem. Theory Comput.*, 2008, 4, 307 and references therein.

t2 E. A. B. Kantchev, T. B. Norsten and M. B. Sullivan, *Org. Biomol. Chem.*, 2012, **10**, 6682.

46 D. A. Pantazis, V. Krewald, M. Orio and F. Neese, *Dalton Trans.*, 2010, **39**, 4959.

**Table S3** Variation in spin densities on the magnetic centers  $[\text{Cr}(\text{Cp}^*)_2]^+$  ( $\text{D}^+$ ) and  $[\text{ETCE}]^-$  ( $\text{A}^-$ ) and coupling constants in the V-pair with  $nk$  points ( $n = 0, 1, 2$ )

Gamma ( $\Gamma$ ) point	n=1	n=2
$J = -7.072 \text{ cm}^{-1}$	$J = -7.501 \text{ cm}^{-1}$	$J = -9.297 \text{ cm}^{-1}$

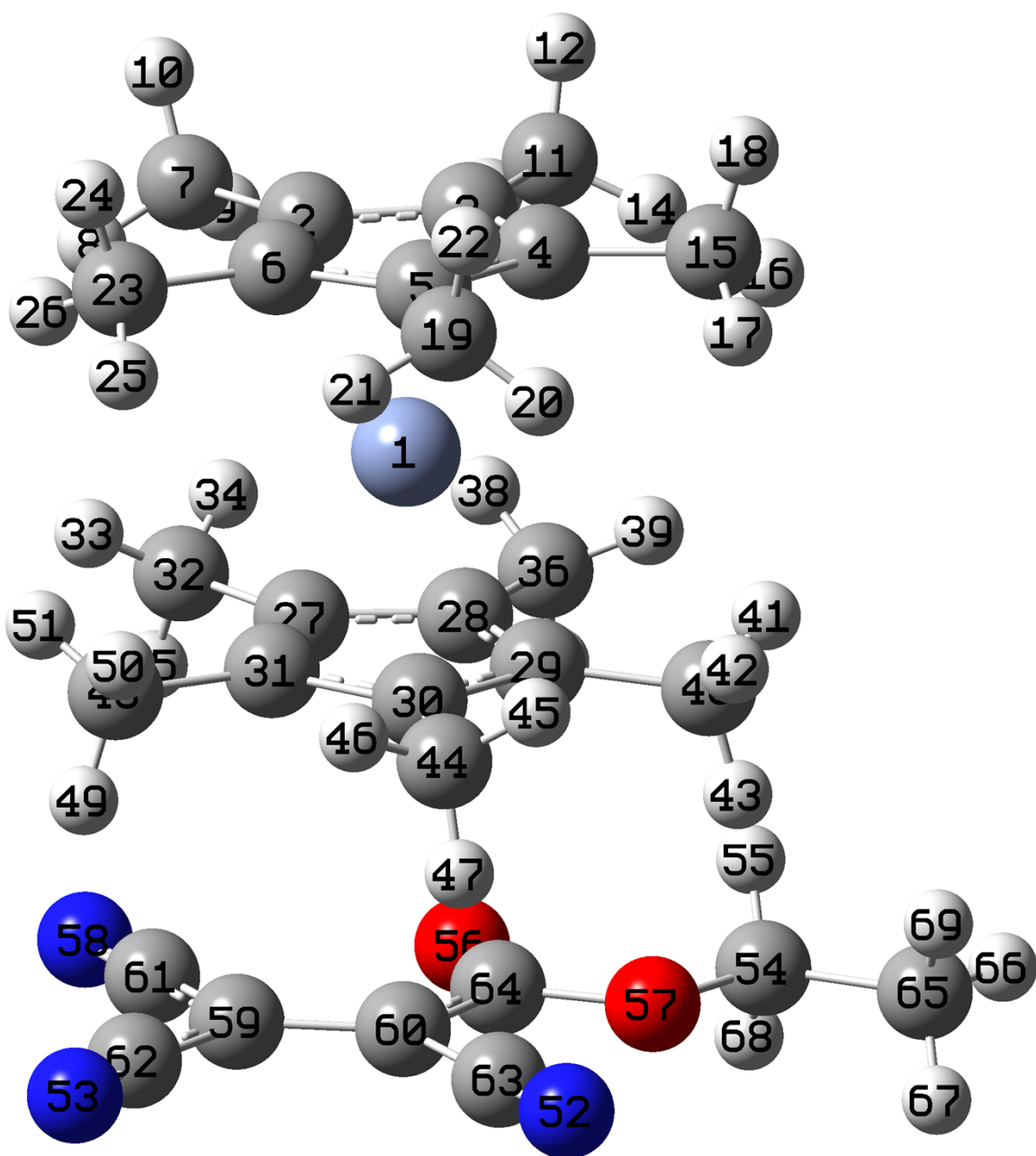
**Table S4** Estimation of magnetic exchange coupling constant with the hybrid PBE0 functional (at PBE1PBE/LANL2DZ level) at **Gamma ( $\Gamma$ ) point** only.

Spin state	Energy in a.u.	$\langle S^2 \rangle^*$	$J$ in $\text{cm}^{-1}$
High spin (quintet)	-1486.6654340	6.100961	-107.24 $\text{cm}^{-1}$
Low spin (triplet)	-1486.6668841	3.133394	

\* The  $\langle S^2 \rangle$  values are obtained through unrestricted density functional approach. The unrestricted density functional calculation leads to the problem of spin contamination. Due to this spin contamination, the  $\langle S^2 \rangle$  value is found to be deviated from the exact value of 6.000.<sup>13, 29a</sup>

t3 (a) D. Bhattacharya and A. Misra, *J. Phys. Chem. A*, 2009, **113**, 5470; (b) S. Shil and A. Misra, *J. Phys. Chem. A*, 2010, **114**, 2022.  
29 (a) S. Paul and A. Misra, *J. Chem. Theory and Comput.*, 2012, **8**, 843.

**Fig. S2** Spin populations of the high-spin states at different functionals.



### Spin populations at UBHandHLYP:

Mulliken atomic spin densities:

		1
1	Cr	3.452088
2	C	-0.075705
3	C	-0.063121
4	C	-0.045285
5	C	-0.052738
6	C	-0.060055
7	C	0.015104
8	H	-0.000610
9	H	-0.000434
10	H	-0.000001
11	C	0.018556
12	H	0.000152
13	H	-0.000172
14	H	-0.001848
15	C	0.030128
16	H	-0.001165
17	H	-0.001640
18	H	0.000560
19	C	0.029040
20	H	-0.002802
21	H	-0.000792
22	H	0.000371
23	C	0.016175
24	H	0.000376
25	H	-0.001354
26	H	-0.000248
27	C	-0.108805
28	C	-0.062361
29	C	-0.021571
30	C	-0.120283
31	C	-0.119003
32	C	0.045692
33	H	0.000664
34	H	-0.002864
35	H	0.004106
36	C	0.082698
37	H	-0.006715
38	H	-0.000653
39	H	0.001546
40	C	-0.001421
41	H	-0.002097

42	H	-0.001464
43	H	-0.003589
44	C	0.031833
45	H	-0.000336
46	H	-0.000281
47	H	-0.001393
48	C	0.012664
49	H	0.006226
50	H	-0.002422
51	H	-0.001617
52	N	0.049340
53	N	0.167389
54	C	-0.004473
55	H	0.002348
56	O	0.099409
57	O	0.017629
58	N	0.223715
59	C	0.484294
60	C	0.408096
61	C	-0.231266
62	C	-0.136223
63	C	-0.085798
64	C	0.020922
65	C	-0.000062
66	H	-0.000062
67	H	-0.000007
68	H	0.001710
69	H	-0.000095

Sum of Mulliken spin densities= 4.00000

### Spin populations at UB3LYP:

Mulliken atomic spin densities:

		1
1	Cr	3.422894
2	C	-0.070972
3	C	-0.069556
4	C	-0.015448
5	C	-0.028181
6	C	-0.065246
7	C	-0.031425
8	H	0.000000
9	H	-0.000386
10	H	0.000826
11	C	0.002208
12	H	0.000927
13	H	0.001524

14	H	-0.001862
15	C	0.043588
16	H	0.000101
17	H	-0.001921
18	H	0.001478
19	C	0.046722
20	H	-0.003167
21	H	0.000387
22	H	0.001457
23	C	-0.001597
24	H	0.001098
25	H	-0.001779
26	H	0.001529
27	C	-0.109473
28	C	-0.067410
29	C	-0.018869
30	C	-0.078382
31	C	-0.099357
32	C	0.024940
33	H	0.000829
34	H	-0.001121
35	H	0.005098
36	C	0.063182
37	H	-0.002777
38	H	-0.000737
39	H	0.001107
40	C	0.002044
41	H	-0.001989
42	H	-0.002236
43	H	-0.002074
44	C	0.028099
45	H	-0.001191
46	H	-0.000268
47	H	0.000027
48	C	0.022861
49	H	0.008220
50	H	-0.002275
51	H	-0.001516
52	N	0.044192
53	N	0.138277
54	C	-0.003654
55	H	0.002692
56	O	0.087095
57	O	0.025861
58	N	0.177527
59	C	0.406035
60	C	0.383816

61	C	-0.148961
62	C	-0.083880
63	C	-0.064732
64	C	0.033645
65	C	0.000030
66	H	-0.000055
67	H	0.000007
68	H	0.002159
69	H	0.000015

Sum of Mulliken spin densities= 4.00000

### Spin populations at UBPW91:

Mulliken atomic spin densities:

1		
1	Cr	3.497814
2	C	-0.079002
3	C	-0.061431
4	C	-0.017070
5	C	-0.048917
6	C	-0.042221
7	C	0.000966
8	H	0.001083
9	H	-0.000175
10	H	0.001815
11	C	0.008819
12	H	0.002314
13	H	0.000647
14	H	-0.001278
15	C	0.020892
16	H	-0.000576
17	H	-0.001608
18	H	0.003239
19	C	0.028673
20	H	-0.002388
21	H	-0.000331
22	H	0.002916
23	C	-0.002179
24	H	0.002718
25	H	-0.000930
26	H	0.000585
27	C	-0.099082
28	C	-0.072920
29	C	-0.008074
30	C	-0.078546
31	C	-0.097472
32	C	0.029235



33	H	-0.000514
34	H	-0.002285
35	H	0.009942
36	C	0.046622
37	H	-0.000098
38	H	-0.000234
39	H	0.000734
40	C	-0.000051
41	H	-0.002295
42	H	-0.001319
43	H	0.000093
44	C	0.017534
45	H	-0.001427
46	H	0.000052
47	H	0.002647
48	C	0.009662
49	H	0.011913
50	H	-0.002621
51	H	-0.001441
52	N	0.041998
53	N	0.122902
54	C	-0.002444
55	H	0.002971
56	O	0.073501
57	O	0.030618
58	N	0.152203
59	C	0.363179
60	C	0.363549
61	C	-0.123714
62	C	-0.074294
63	C	-0.063803
64	C	0.036157
65	C	-0.000035
66	H	-0.000044
67	H	0.000021
68	H	0.002749
69	H	0.000057

Sum of Mulliken spin densities= 4.00000

### Spin populations at UPBEPBE:

Mulliken atomic spin densities:

	1	
1	Cr	3.482349
2	C	-0.079710
3	C	-0.061431
4	C	-0.019050

5	C	-0.049505
6	C	-0.045477
7	C	0.003530
8	H	0.000893
9	H	-0.000254
10	H	0.001772
11	C	0.011471
12	H	0.002181
13	H	0.000512
14	H	-0.001491
15	C	0.024189
16	H	-0.000790
17	H	-0.001639
18	H	0.002998
19	C	0.030139
20	H	-0.002610
21	H	-0.000518
22	H	0.002711
23	C	0.001324
24	H	0.002596
25	H	-0.000923
26	H	0.000473
27	C	-0.099427
28	C	-0.073288
29	C	-0.013328
30	C	-0.074590
31	C	-0.097222
32	C	0.030814
33	H	-0.000503
34	H	-0.001860
35	H	0.008246
36	C	0.046666
37	H	-0.000198
38	H	-0.000088
39	H	0.000593
40	C	0.002529
41	H	-0.002138
42	H	-0.001258
43	H	0.000057
44	C	0.022720
45	H	-0.001098
46	H	0.000025
47	H	0.002193
48	C	0.015856
49	H	0.010309
50	H	-0.002223
51	H	-0.001255

52	N	0.040037
53	N	0.119247
54	C	-0.003156
55	H	0.002989
56	O	0.072985
57	O	0.031814
58	N	0.148111
59	C	0.346273
60	C	0.359469
61	C	-0.117480
62	C	-0.061239
63	C	-0.054212
64	C	0.037033
65	C	0.000092
66	H	-0.000062
67	H	0.000030
68	H	0.002712
69	H	0.000086

Sum of Mulliken spin densities= 4.00000

### Spin populations at UTPSSH:

Mulliken atomic spin densities:

		1
1	Cr	3.464734
2	C	-0.054405
3	C	-0.044560
4	C	-0.047904
5	C	-0.042815
6	C	-0.038004
7	C	0.011884
8	H	0.000870
9	H	0.000727
10	H	0.001958
11	C	0.011298
12	H	0.002626
13	H	0.000849
14	H	-0.000066
15	C	0.019427
16	H	0.000241
17	H	0.000004
18	H	0.003762
19	C	0.023956
20	H	0.000871
21	H	-0.000325
22	H	0.003637
23	C	0.010978

24	H	0.002765
25	H	0.000957
26	H	0.000540
27	C	-0.063604
28	C	-0.062070
29	C	-0.044298
30	C	-0.106347
31	C	-0.104426
32	C	0.015345
33	H	0.001561
34	H	-0.001529
35	H	0.008415
36	C	0.059519
37	H	0.001095
38	H	-0.001258
39	H	0.002935
40	C	-0.020066
41	H	-0.002158
42	H	-0.001029
43	H	0.001698
44	C	-0.000268
45	H	-0.000443
46	H	-0.000173
47	H	0.004056
48	C	-0.011148
49	H	0.010281
50	H	-0.000032
51	H	-0.001941
52	N	0.044756
53	N	0.140977
54	C	-0.004794
55	H	0.002717
56	O	0.083690
57	O	0.026843
58	N	0.178566
59	C	0.415879
60	C	0.412997
61	C	-0.170125
62	C	-0.098821
63	C	-0.079362
64	C	0.026171
65	C	0.000083
66	H	-0.000061
67	H	0.000003
68	H	0.002342
69	H	0.000021

Sum of Mulliken atomic spin densities = 4.00000