Electronic Supplementary Material (ESI) for RSC Advances.

Supporting information

Table S1 The most positive electrostatic potential (V_{max}, kcal/mol) on the ring central point in the π molecule at the 0.001 electrons $Bohr^{-3}$ of the monomers (**1-3**) and dyads (**13-21**) as well as its difference between them (ΔV_{max}, kcal/mol).

	V_{max}	ΔV_{max}
1	4.58	---
2	10.18	---
3	12.11	---
13	56.35	51.77
14	57.17	52.59
15	55.97	51.39
16	40.54	30.36
17	41.98	31.80
18	40.35	30.17
19	52.08	39.97
20	50.83	38.72
21	50.20	38.09

Table S2 The most negative electrostatic potential (V_{min}, kcal/mol) at the N/O atomic surface of the π molecule at the 0.001 electrons $Bohr^{-3}$ in the monomers (**1-3**) and dyads (**4-12**) as well as its difference between them (ΔV_{min}, kcal/mol).

	V_{min}	ΔV_{min}
1	-29.62	---
2	-30.56	---
3	-26.10	---
4	-103.54	-73.92
5	-99.15	-69.53
6	-97.26	-67.65
7	-87.60	-57.04
8	-84.59	-54.03
9	-83.65	-53.09
10	-99.15	-73.04
11	-90.99	-64.88
12	-89.73	-63.63

Table S3 Second-order perturbation energies (E^2, kcal/mol) for the metal-Lp interaction in the complexes **13-21** at the HF/aug-cc-pVDZ(PP) level.

Complexes	$E^2(1)$	$E^2(2)$	$E^2(3)$
13(**1**+2CuCN)	15.41	103.62	3.76
14(**1**+2AgCN)	21.40	11.32	2.80
15(**1**+2AuCN)	46.83	15.49	5.94
16(**2**+2CuCN)	11.70	119.66	6.80
17(**2**+2AgCN)	27.59	32.65	4.75
18(**2**+2AuCN)	78.00	29.04	10.02
19(**3**+2CuCN)	6.40	95.41	3.85
20(**3**+2AgCN)	17.28	16.14	2.02
21(**3**+2AuCN)	53.34	8.85	4.43

Note: $E^2(1)$, $E^2(2)$, and $E^2(3)$ correspond to the orbital interactions of $Lp_{(N/O)} \rightarrow BD^*_{(C-M)}$, $Lp_{(N/O)} \rightarrow Lp^*_{(M)}$, and $Lp_{(M)} \rightarrow BD^*_{(C-N/C-O)}$, respectively.

Table S4 Interaction energy of the anion-metal interaction (ΔE_{far}, kcal/mol) and equilibrium distances (R, Å) in the complexes **22-46** as well as their changes (ΔR, Å) relative to the complexes **4-21**

Complexes	R_1	R_2	ΔR_1	ΔR_2	ΔE_{far}
22	2.372	1.846	-0.291	0.003	-38.25
23	2.377	2.074	-0.286	-0.016	-36.62
24	2.364	2.027	-0.300	-0.006	-33.04
25	2.904	1.846	-0.336	0.003	-32.52
26	2.907	2.077	-0.333	-0.013	-31.73
27	2.893	2.027	-0.348	-0.005	-28.26
28	3.056	1.845	-0.338	0.002	-31.18
29	3.057	2.077	-0.338	-0.013	-30.65
30	3.041	2.027	-0.353	-0.006	-27.34
31	2.428	1.790	-0.144	0.013	-18.66
32	2.430	2.032	-0.142	-0.006	-18.10
33	2.425	1.980	-0.147	0.006	-15.16
34	2.982	1.789	-0.165	0.012	-17.11
35	2.984	2.034	-0.163	-0.004	-16.68
36	2.982	1.979	-0.165	0.005	-13.81
37	3.141	1.789	-0.159	0.011	-16.63
38	3.148	2.034	-0.152	-0.004	-16.25
39	3.139	1.979	-0.161	0.005	-13.40
40	1.653	1.801	-0.564	-0.007	-35.43
41	1.640	2.079	-0.577	-0.040	-42.38
42	1.438	2.058	-0.779	-0.006	-32.38
43	2.596	1.801	-0.415	-0.006	-25.91
44	2.636	2.077	-0.375	-0.042	-23.91
45	2.617	2.041	-0.394	-0.023	-21.36
46	2.767	1.800	-0.429	-0.007	-24.65
47	2.810	2.076	-0.386	-0.043	-22.61
48	2.727	2.052	-0.469	-0.012	-20.17

Table S5 Charge transfer in the anion-π (CT_1, e) and metal-Lp (CT_2, e) interactions in the complexes **22-46** as well as their changes (ΔCT, e) relative to the complexes **4-21**.

Complexes	CT_1	CT_2	ΔCT_1	ΔCT_2
22	0.0321	0.2654	0.0226	0.0396
23	0.0298	0.2266	0.0203	0.0412
24	0.0328	0.3398	0.0233	0.0654
25	0.0463	0.2548	0.0389	0.0290
26	0.0413	0.2148	0.0339	0.0294
27	0.0493	0.3248	0.0419	0.0504
28	0.0561	0.2532	0.0486	0.0274
29	0.0494	0.2130	0.0419	0.0276
30	0.0607	0.3224	0.0532	0.0480
31	0.0088	0.2630	0.0044	0.0378
32	0.0084	0.2002	0.0040	0.0360
33	0.0089	0.2886	0.0045	0.0564
34	0.0102	0.2568	0.0055	0.0316
35	0.0098	0.1940	0.0051	0.0298
36	0.0104	0.2802	0.0057	0.0480
37	0.0110	0.2550	0.0062	0.0298
38	0.0105	0.1926	0.0057	0.0284
39	0.0113	0.2780	0.0065	0.0458
40	0.2220	0.2282	0.1697	0.0540
41	0.2213	0.1522	0.1690	0.0518
42	0.3535	0.2682	0.3012	0.1204
43	0.1348	0.2134	0.1057	0.0392
44	0.1147	0.1372	0.0856	0.0368
45	0.1314	0.2026	0.1023	0.0548
46	0.1523	0.2132	0.1240	0.0390
47	0.1276	0.1378	0.0993	0.0374
48	0.1875	0.2282	0.1592	0.0804

Note: CT_1 is the sum of **1** and the charge of the anion in the anion-π interaction and CT_2 is the absolute value of the sum of charge on all atoms of MCN in the metal-Lp interaction.

Table S6 Change of occupancy (Δn, e) on the selected orbitals in the multicomponent systems (**22-48**) as well as the isolated anion-π and metal-Lp complexes (in parentheses) compared with monomers

Complexes	$\Delta n_{N/O}$	Δn_{M}	$\Delta n^{*}_{C\text{-}M}$
22	-0.1149(-0.1049)	-0.0107(-0.0136)	0.0229(0.0212)
23	-0.0953(-0.0803)	-0.0107(-0.0115)	0.0393(0.0374)
24	-0.1621(-0.1431)	-0.0167(-0.0197)	0.0621(0.0574)
25	-0.1114	-0.0111	0.0230
26	-0.0906	-0.0107	0.0388
27	-0.1570	-0.0171	0.0609
28	-0.1109	-0.0112	0.0231
29	-0.0898	-0.0108	0.0388
30	-0.1562	-0.0172	0.0608
31	-0.1525(-0.1470)	0.0094(-0.0158)	0.0162(0.0161)
32	-0.1176(-0.1081)	-0.0123(-0.0136)	0.0350(0.0341)
33	-0.1832(-0.1729)	-0.0195(-0.0236)	0.0558(0.0539)
34	-0.1515	-0.0131	0.0161
35	-0.1162	-0.0124	0.0347
36	-0.1815	-0.0199	0.0554
37	-0.1512	-0.0132	0.0160
38	-0.1158	-0.0124	0.0347
39	-0.1811	-0.0200	0.0553
40	-0.0537(-0.0374)	-0.0092(-0.0145)	0.0108(0.0098)
41	-0.0127(-0.0003)	-0.0063(-0.0088)	0.0287(0.0236)
42	-0.0019(-0.0373)	-0.0115(-0.0166)	0.0497(0.0549)
43	-0.0490	-0.0109	0.0106
44	-0.0133	-0.0090	0.0273
45	-0.0720	-0.0146	0.0665
46	-0.0497	-0.0112	0.0106
47	-0.0129	-0.0090	0.0274
48	-0.1823	-0.0072	0.0778

Figure S1 Relationship between the change of charge transfer and the cooperative energy.