Electronic Supporting Information

Self-assembly properties of zinc(II) complexes with azo ligands grafted with the dodecyl chains: towards supramolecular materials driven by coordination and hydrophobic effect

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Table S1 Crystal and structure refinement data for **1** and **2**.

Compound	**1**	**2**
Formula	$C_{44}H_{64}N_{10}O_8Zn$	$C_{58}H_{84}N_6O_{14}Zn_3$
Formula weight, g mol^{-1}	926.44	1285.48
Crystal size, mm^3	0.26 × 0.25 × 0.10	0.12 × 0.09 × 0.05
Crystal system	Monoclinic	Triclinic
Space group	*C*2/*c*	$P\bar{1}\bar{1}$
a, Å	15.459(2)	9.8122(12)
b, Å	10.6509(13)	10.5321(13)
c, Å	30.001(4)	14.9799(17)
α, °	-	87.605(4)
β, °	103.017(6)	87.231(4)
γ, °	-	86.746(4)
V, Å^3	4812.8(11)	1542.6(3)
Z	4	1
F(000)	1968	676
μ, mm^{-1}	0.57	1.223
ρ_c, g cm^{-3}	1.279	1.384
T, K	295(2)	150(2)
ϑ range, º	2.35–27.18	2.33–27.02
Index ranges, *h*, *k*, *l*	–20→20 –13→13 –38→38	–12→12 –13→13 –18→19
Reflections collected/unique	30275/5492	23386/7060
Data/restraints/parameters	4483/0/285	5577/0/371
R indices [$I > 2\sigma(I)$]	$R = 0.062$, $R_w = 0.1695^*$	$R = 0.0343$, $R_w = 0.864^{**}$
R indices (all data)	$R = 0.0751$, $R_w = 0.1788$	$R = 0.0506$, $R_w = 0.096$
Goodness-of-fit	1.088	0.948
R_{int}	0.0646	0.0488
$\Delta\rho_{max}$, $\Delta\rho_{min}$, e Å^{-3}	0.7, –0.467	0.4, –0.44

$^*w = 1 / [\sigma^2(F_o^2) + (0.0856 \cdot P)^2 + 5.3972 \cdot P]$ where $P = (F_o^2 + 2 \cdot F_c^2) / 3$.

$^{**}w = 1 / [\sigma^2(F_o^2) + (0.0600 \cdot P)^2]$ where $P = (F_o^2 + 2 \cdot F_c^2) / 3$.

Table S2 Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

Complex **1**			
Bond		Angle	
Zn(1)–O(2), O(2_a)	2.0327(3)	O(2)–Zn(1)–N(1_a), N(1)–Zn(1)–O(2_a)	90.12(1)
Zn(1)–N(1), N(1_a)	2.0646(3)		
Zn(1)–N(4), N(4_a)	2.4923(3)	O(2)–Zn(1)–N(4_a), N(4)–Zn(1)–O(2_a)	152.70(1)
Angle			
O(2)–Zn(1)–N(1), O(2_a)–Zn(1)–N(1_a)	105.15(1)	N(1)–Zn(1)–N(4), N(1_a)–Zn(1)–N(4_a)	68.58(1)
O(2)–Zn(1)–N(4), O(2_a)–Zn(1)–N(4_a)	88.27(1)	N(1)–Zn(1)–N(4_a), N(4)–Zn(1)–N(1_a)	88.76(1)
O(2)–Zn(1)–O(2_a)	114.54(1)	N(1)–Zn(1)–N(1_a)	151.80(1)
		N(4)–Zn(1)–N(4_a)	74.89(1)
Complex **2**			
Bond		Angle	
Zn(1)–O(1)	2.0023(17)	O(4)–Zn(1)–N(1)	147.79(6)
Zn(1)–O(3)	2.4600(17)	O(4)–Zn(1)–N(3)	93.23(6)
Zn(1)–O(4)	2.0211(15)	O(5)–Zn(1)–N(1)	102.46(7)
Zn(1)–O(5)	1.9805(16)	O(5)–Zn(1)–N(3)	88.49(6)
Zn(1)–N(1)	2.0813(18)	N(1)–Zn(1)–N(3)	71.90(7)
Zn(1)–N(3)	2.3486(18)	O(2)–Zn(2)–O(4), O(2_a)–Zn(2)–O(4_a)	91.18(6)
Zn(2)–O(2), O(2_a)	2.1201(15)		
Zn(2)–O(4), O(4_a)	2.0936(14)	O(2)–Zn(2)–O(6), O(2_a)–Zn(2)–O(6_a)	91.55(6)
Zn(2)–O(6), O(6_a)	2.0846(15)		
Angle		O(2)–Zn(2)–O(2_a), O(4)–Zn(2)–O(4_a), O(6)–Zn(2)–O(6_a)	180.00
O(1)–Zn(1)–O(3)	95.03(6)		
O(1)–Zn(1)–O(4)	97.39(6)		
O(1)–Zn(1)–O(5)	101.24(7)	O(2)–Zn(2)–O(4_a), O(4)–Zn(2)–O(2_a)	88.82(6)
O(1)–Zn(1)–N(1)	92.31(7)		
O(1)–Zn(1)–N(3)	163.05(6)	O(2)–Zn(2)–O(6_a), O(6)–Zn(2)–O(2_a)	88.45(6)
O(3)–Zn(1)–O(4)	57.31(5)		
O(3)–Zn(1)–O(5)	158.08(6)	O(4)–Zn(2)–O(6), O(4_a)–Zn(2)–O(6_a)	88.94(6)
O(3)–Zn(1)–N(1)	91.37(6)		
O(3)–Zn(1)–N(3)	79.64(6)	O(4)–Zn(2)–O(6_a), O(6)–Zn(2)–O(4_a)	91.06(6)
O(4)–Zn(1)–O(5)	105.61(6)		

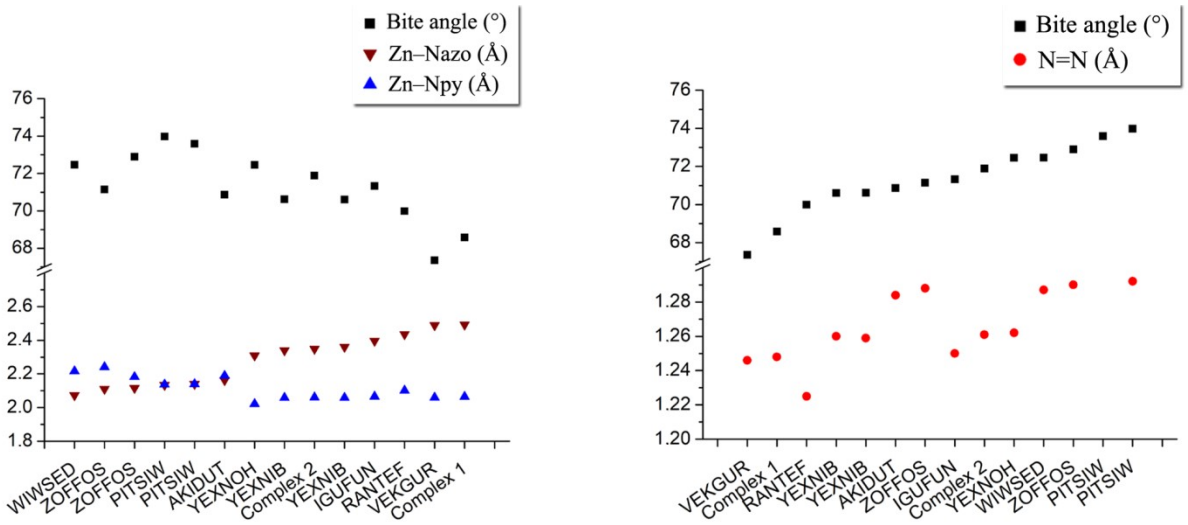

Fig. S1 Evolution of the bite angle with the Zn−N distances (left) and evolution of the N=N distance with the bite angle (right) in Zn azpm and Zn azpy complexes from the CCDC structures.

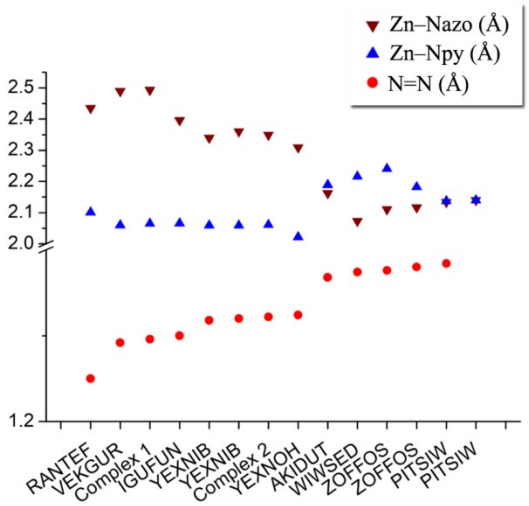

Fig. S2 Evolution of the N=N distance with the Zn−Nazo and Zn−Npy distances in Zn azpm and Zn azpy complexes from the CCDC structures.

Table S3 Selected bond lengths (Å) of optimized complex **1** geometries at different levels of theory compared to crystal structure data as referent values[a]

	Level of theory / Bond	Zn(1)–O(2)	Zn(1)–N(1)	Zn(1)–N(4)
		2.0327[a]	2.0646[a]	2.4923[a]
1	PBE1PBE / 6-31G	2.0139	2.0991	2.4487
2	PBE1PBE / 6-311G	2.0453*	2.1140*	2.2778*
3	PBE1PBE / def2TZVP	2.0085	2.1455	2.5808
4	B3LYP / 6-31G	2.0205	2.1187	2.4992
5	B3LYP / 6-311G	2.0555*	2.1265*	2.3292*
6	B3LYP / lanl2dz	2.0701*	2.1717*	2.3889*
7	B3LYP / 6-31G(d,p) for C, O, N, H LanL2DZ for Zn	2.1366*	2.2508*	2.7967*
8	B3LYP / 6-31+G(d,p) for O 6-31G(d) for C, N 6-31G for H 6-311+G(d,p) for Zn	2.0240	2.1387*	2.5254*
9	B3LYP / 6-31+G(d,p) for O, N 6-31G(d) for C 6-31G for H 6-311+G(d,p) for Zn	2.0199	2.1544	2.6093
10	B3PW91 / 6-311G(d,p)	2.0016	2.1283	2.4203
11	BVP86 / 6-31G	2.0254*	2.1058*	2.4579*
12	TPSSTPSS / 6-31G	2.0172	2.0990	2.4419*
13	WB97XD / 6-31G	2.0080*	2.1052*	2.4517*
14	mPW1PW91 / 6-31G	2.0102	2.0976	2.4530
15	LC-wPBE / 6-31G	1.9955	2.0824	2.4407
16	LC-wPBE / 6-311G(d,p)	1.9853	2.1139	2.3907
17	M06-2X / 6-31G	2.0606*	2.1295*	2.4383*
18	CAM-B3LYP / 6-31G	2.0033*	2.0980*	2.4545*
19	CAM-B3LYP / 6-311G	2.0352	2.1115	2.2890*
20	CAM-B3LYP / 6-311G(d,p)	1.9902	2.1246	2.4144

* average value

Table S4 Selected angles (°) of optimized complex **1** geometries at different levels of theory compared to crystal structure data as referent values[a]

Angle / Level of theory			MPW1PW91 6-31G	B3LYP 6-31G	BVP86 6-31G	TPSSTPSS 6-31G	CAM-B3LYP 6-311G(d,p)
N1–Zn1–N4, N1_a–Zn1–N4_a	*cis*	68.58[a]	69.12	68.70	69.47	69.52	68.56
N4–Zn1–N4_a	*cis*	74.89[a]	77.79	81.23	81.70	77.07	76.96
O2–Zn1–N4, O2_a–Zn1–N4_a	*cis*	88.27[a]	88.20	87.71	87.30	87.28	85.92
N1–Zn1–N4_a, N4–Zn1–N1_a	*cis*	88.76[a]	89.30	89.20	88.86	88.74	92.70
O2–Zn1–N1_a, N1–Zn1–O2_a	*cis*	90.12[a]	84.99	85.15	84.20	84.10	86.97
O2–Zn1–N1_a, N1–Zn1–O2_a	*cis*	105.15[a]	110.02	111.06	111.75	110.47	104.85
O2–Zn1–O2_a	*cis*	114.54[a]	114.80	112.85	113.29	117.44	119.71
N1–Zn1–N1_a	*trans*	151.80[a]	152.60	151.23	151.63	152.50	156.63
O2–Zn1–N4_a, N4–Zn1–O2_a	*trans*	152.70[a]	150.43	151.59	151.52	149.31	149.02

Table S5 Selected bond lengths (Å) of optimized complex **2** geometries at different levels of theory compared to crystal structure data as referent values[a]

Bond / Level of theory		B3LYP 6-31G	B3LYP 6-311G	B3LYP 6-311G(d,p)	B3LYP 6-311G, lanl2dz	CAM-B3LYP 6-311G(d,p)
Zn(1)–O(1)	2.0023[a]	2.048	2.037	2.032	2.059	2.012
Zn(1)–O(3)	2.4600[a]	2.748	2.578	2.330	2.401	2.411
Zn(1)–O(4)	2.0211[a]	2.012	2.039	2.076	2.129	2.020
Zn(1)–O(5)	1.9805[a]	1.988	1.996	1.999	2.037	1.979
Zn(1)–N(1)	2.0813[a]	2.067	2.063	2.103	2.141	2.075
Zn(1)–N(3)	2.3486[a]	2.333	2.319	2.346	2.383	2.315
Zn(2)–O(2), O(2_a)	2.1201[a]	2.127	2.113	2.104	2.152	2.098
Zn(2)–O(4), O(4_a)	2.0936[a]	2.011	2.039	2.077	2.129	2.020
Zn(2)–O(6), O(6_a)	2.0846[a]	2.113	2.111	2.104	2.136	2.083

Table S6 The calculated natural atomic charges (NACs) and natural electron configurations (NECs) of selected atoms in free molecules/ions and complex **1**

Atoms	Free molecule/ion	Complex **1***
NACs		
L^1: $N(1)_{pm}$	–0.4826	−0.6421
L^1: $N(4)_{azo}$	–0.1445	−0.2181
$O(2)_{NO3}$	–0.5852	−0.7625
Zn(1)	/	+1.6907
NECs**		
L^1: $N(1)_{pm}$	[core]$2s^{1.37}$ $2p^{4.10}$ $3p^{0.01}$ $3d^{0.01}$	[core]$2s^{1.35}$ $2p^{4.27}$ $3p^{0.02}$
L^1: $N(4)_{azo}$	[core]$2s^{1.40}$ $2p^{3.72}$ $3s^{0.01}$ $3p^{0.01}$ $3d^{0.01}$	[core]$2s^{1.37}$ $2p^{3.81}$ $3s^{0.01}$ $3p^{0.02}$ $3d^{0.01}$
$O(2)_{NO3}$	[core]$2s^{1.76}$ $2p^{4.81}$	[core]$2s^{1.77}$ $2p^{4.98}$ $3p^{0.01}$
Zn(1)	/	[core]$4s^{0.33}$ $3d^{9.96}$ $4p^{0.01}$ $5s^{0.01}$

* Half of the data were presented due to symmetry consideration

** [core] represent inner core electrons

Table S7 The calculated natural atomic charges (NACs) and natural electron configurations (NECs) of selected atoms in free molecules/ions and complex **2**

Atoms	Free molecule/ion	Complex **2***
NACs		
L^2: $N(1)_{py}$	−0.4506	−0.6140
L^2: $N(3)_{azo}$	−0.1461	−0.2156
$O(3)_{ac}$	−0.7979	−0.7135
$O(5)_{ac}$	−0.8084	−0.8696
$O(4)_{ac}$	−0.8084	−0.9814
Zn(1)	/	+1.6826
$O(6)_{ac}$		−0.8298
$O(2)_{ac}$		−0.8160
Zn(2)	/	+1.7313
NECs**		
L^2: $N(1)_{py}$	[core]$2s^{1.35}$ $2p^{4.08}$ $3p^{0.01}$ $3d^{0.01}$	[core]$2s^{1.34}$ $2p^{4.25}$ $3p^{0.02}$
L^2: $N(3)_{azo}$	[core]$2s^{1.39}$ $2p^{3.73}$ $3s^{0.01}$ $3p^{0.01}$ $3d^{0.01}$	[core]$2s^{1.36}$ $2p^{3.81}$ $3s^{0.01}$ $3p^{0.02}$ $3d^{0.01}$
$O(4)_{ac}$	[core]$2s^{1.71}$ $2p^{5.08}$	[core]$2s^{1.70}$ $2p^{5.16}$ $3p^{0.01}$
$O(3)_{ac}$	[core]$2s^{1.71}$ $2p^{5.07}$	[core]$2s^{1.70}$ $2p^{5.00}$
$O(5)_{ac}$	[core]$2s^{1.71}$ $2p^{5.08}$	[core]$2s^{1.70}$ $2p^{5.16}$ $3p^{0.01}$
Zn(1)	/	[core]$4s^{0.33}$ $3d^{9.97}$ $4p^{0.01}$
Zn(2)	/	[core]$4s^{0.28}$ $3d^{9.98}$ $4p^{0.01}$

* Half of the data are presented due to symmetry consideration

** [core] represent inner core electrons

Table S8 Selected Donor NBO(i) and Acceptor NBO(j) Orbitals in Complexes, Orbital Occupancy (Occ.), Percent of Atomic Orbitals Contribute to NBOs (AO%) and the Second Order Perturbative Energies E^2 (kcal mol^{-1}) corresponding to donor-acceptor interactions in complexes

	Donor			Acceptor		
NBO(i)	Occ.	AO%	NBO(j)	Occ.	AO%	E^2
complex **1**						
LP(2) $O(2)_{NO3}$	1.9075	s(24.00)p(75.98)	LP*(6)Zn	0.3293	s(99.85)p(0.01)d(0.13)	38.67
LP(1) $O(2)_{NO3}$	1.9665	s(54.29)p(45.69)	LP*(6)Zn	0.3293	s(99.85)p(0.01)d(0.13)	9.89
LP(1) $N(1)_{pm}$	1.8941	s(24.33)p(75.65)	LP*(6)Zn	0.3293	s(99.85)p(0.01)d(0.13)	30.14
LP(1) $N(4)_{azo}$	1.9277	s(33.21)p(66.76)	LP*(6)Zn	0.3293	s(99.85)p(0.01)d(0.13)	17.88
complex **2**					Zn(1) center	
LP(1) $N(1)_{py}$	1.8891	s(23.69)p(76.29)	LP*(6)Zn	0.3330	s(99.90)p(0.07)d(0.03)	32.83
LP(1) $N(3)_{azo}$	1.9273	s(32.68)p(67.29)	LP*(6)Zn	0.3330	s(99.90)p(0.07)d(0.03)	21.22
LP(1) $O(1)_{ac}$	1.9516	s(48.54)p(51.43)	LP*(6)Zn	0.3330	s(99.90)p(0.07)d(0.03)	13.10
LP(2) $O(4)_{ac}$	1.8911	s(10.26)p(89.72)	LP*(6)Zn	0.3330	s(99.90)p(0.07)d(0.03)	30.61
LP(2) $O(4)_{ac}$	1.8955	s(16.33)p(83.65)	LP*(6)Zn	0.3330	s(99.90)p(0.07)d(0.03)	30.95
LP(1) $O(4)_{ac}$	1.9381	s(44.41)p(55.58)	LP*(6)Zn	0.3330	s(99.90)p(0.07)d(0.03)	4.63
LP(1) $O(3)_{ac}$	1.9684	s(56.03)p(43.95)	LP*(6)Zn	0. 3330	s(99.90)p(0.07)d(0.03)	4.68
LP(2) $O(5)_{ac}$	1.8871	s(12.37)p(87.61)	LP*(6)Zn	0. 3330	s(99.90)p(0.07)d(0.03)	34.10
LP(1) $O(5)_{ac}$	1.9540	s(46.32)p(53.66)	LP*(6)Zn	0. 3330	s(99.90)p(0.07)d(0.03)	12.51
					Zn(2) center	
LP(1) $O(2)_{ac}$	1.9493	s(53.05)p(46.93)	LP*(6)Zn	0.2827	s(99.99)d(0.01)	17.32
LP(2) $O(2)_{ac}$	1.8950	s(4.76)p(95.21)	LP*(6)Zn	0.2827	s(99.99)d(0.01)	16.17
LP(1) $O(4)_{ac}$	1.9381	s(44.41)p(55.58)	LP*(6)Zn	0.2827	s(99.99)d(0.01)	23.79
LP(1) $O(6)_{ac}$	1.9490	s(52.38)p(47.60)	LP*(6)Zn	0.2827	s(99.99)d(0.01)	17.50
LP(2) $O(6)_{ac}$	1.8963	s(5.17)p(94.81)	LP*(6)Zn	0.2827	s(99.99)d(0.01)	16.45

LP(1) and (2) denote the first and second lone electron pair orbital

LP*(6) denote the sixth-center orbital with an anti-bonding character.

Table S9 Topological parameters of electron density for free ligand L^1 and its complex **1**: electron density (ρ(r)), Laplacian distribution ($\nabla^2\rho$(r)), potential energy density (V(r)), kinetic energy density (G(r)), and electronic energy density (H(r)) at the Bond Critical Points (3, −1). Parameters are all in the atomic unit (a.u) except k(r) = |V(r)| / G(r).

Bond	ρ(r)	$\nabla^2\rho$(r)	H(r)	V(r)	G(r)	k(r)
free ligand						
$C(1)_{pm}$–$N(1)_{pm}$	0.3536	−1.0811	−0.5044	−0.7384	0.2341	3.1547
$N(1)_{pm}$– $C(2)_{pm}$	0.3472	−1.0032	−0.5059	−0.7609	0.2551	2.9833
$C(2)_{pm}$–$C(3)_{pm}$	0.3173	−0.9158	−0.3325	−0.4361	0.1036	4.2101
$C(3)_{pm}$–$C(4)_{pm}$	0.3173	−0.9162	−0.3326	−0.4361	0.1035	4.2129
$C(4)_{pm}$–$N(2)_{pm}$	0.3479	−1.0044	−0.5077	−0.7643	0.2566	2.9786
$N(2)_{pm}$–$C(1)_{pm}$	0.3537	−1.0927	−0.5055	−0.7377	0.2323	3.1760
$C(1)_{pm}$–$N(3)_{azo}$	0.3046	−0.9296	−0.3474	−0.4624	0.1150	4.0212
$N(3)_{azo}$–$N(4)_{azo}$	0.4767	−1.2475	−0.6052	−0.8984	0.2933	3.0634
$N(4)_{azo}$–$C(5)_{ph}$	0.2991	−0.8885	−0.3708	−0.5195	0.1487	3.4936
complex **1**						
Zn(1)–$N(1)_{pm}$	0.0654	0.2469	−0.0134	−0.0885	0.0751	1.1781
Zn(1)–$N(4)_{azo}$	0.0348	0.1170	−0.0049	−0.0391	0.0342	1.1435
Zn(1)–$O(2)_{NO3}$	0.0779	0.4021	−0.0091	−0.1188	0.1097	1.0834
$C(1)_{pm}$–$N(1)_{pm}$	0.3488	−1.0233	−0.5032	−0.7507	0.2474	3.0339
$N(1)_{pm}$– $C(2)_{pm}$	0.3375	−0.8770	−0.4963	−0.7733	0.2770	2.7915
$C(2)_{pm}$–$C(3)_{pm}$	0.3190	−0.9307	−0.3360	−0.4394	0.1034	4.2505
$C(3)_{pm}$–$C(4)_{pm}$	0.3186	−0.9247	−0.3350	−0.4389	0.1039	4.2255
$C(4)_{pm}$–$N(2)_{pm}$	0.3458	−1.0010	−0.5038	−0.7573	0.2535	2.9872
$N(2)_{pm}$–$C(1)_{pm}$	0.3612	−1.1293	−0.5217	−0.7611	0.2394	3.1794
$C(1)_{pm}$–$N(3)_{azo}$	0.3023	−0.9026	−0.3405	−0.4553	0.1148	3.9652
$N(3)_{azo}$–$N(4)_{azo}$	0.4736	−1.2308	−0.5969	−0.8861	0.2892	3.0640
$N(4)_{azo}$–$C(5)_{ph}$	0.2964	−0.8378	−0.3879	−0.5664	0.1785	3.1734

Table S10 Topological parameters of electron density for free ligand L^2 and its complex **2**: electron density (ρ(r)), Laplacian distribution ($\nabla^2\rho$(r)), potential energy density (V(r)), kinetic energy density (G(r)), and electronic energy density (H(r)) at the Bond Critical Points (3, −1). Parameters are all in the atomic unit (a.u) except k(r) = |V(r)| / G(r).

Bond	ρ(r)	$\nabla^2\rho$(r)	H(r)	V(r)	G(r)	k(r)
free ligand						
$C(1)_{py}$–$N(1)_{py}$	0.3502	−1.0395	−0.5045	−0.7491	0.2446	3.0624
$N(1)_{py}$–$C(5)_{py}$	0.3458	−0.9559	−0.5074	−0.7759	0.2685	2.8901
$C(5)_{py}$–$C(4)_{py}$	0.3146	−0.8999	−0.3262	−0.4275	0.1012	4.2220
$C(4)_{py}$–$C(3)_{py}$	0.3136	−0.8961	−0.3259	−0.4279	0.1019	4.1977
$C(3)_{py}$–$C(2)_{py}$	0.3158	−0.9085	−0.3306	−0.4341	0.1035	4.1949
$C(2)_{py}$–$C(1)_{py}$	0.3159	−0.9091	−0.3280	−0.4287	0.1007	4.2562
$C(1)_{py}$–$N(2)_{azo}$	0.2983	−0.8915	−0.3432	−0.4635	0.1203	3.8522
$N(2)_{azo}$–$N(3)_{azo}$	0.4765	−1.2491	−0.6039	−0.8956	0.2917	3.0707
$N(3)_{azo}$–$C(6)_{ph}$	0.2995	−0.8911	−0.3689	−0.5149	0.1461	3.5251
complex **2**						
Zn(1) centre						
Zn(1)–$N(1)_{py}$	0.0725	0.2930	−0.0015	−0.1027	0.0880	1.1672
Zn(1)–$N(3)_{azo}$	0.0436	0.1457	−0.0078	−0.0520	0.0442	1.1763
Zn(1)–$O(3)_{ac}$	0.0304	0.1203	−0.0022	−0.0345	0.0323	1.0681
Zn(1)–$O(4)_{ac}$	0.0740	0.3603	−0.0102	−0.1105	0.1003	1.1017
Zn(1)–$O(5)_{ac}$	0.0785	0.4154	−0.0092	−0.1222	0.1130	1.0810
Zn(1)–$O(1)_{ac}$	0.0727	0.3683	−0.0087	−0.1094	0.1007	1.0859
Zn(2) centre						
Zn(2)–$O(6)_{ac}$	0.0592	0.2840	−0.0068	−0.0847	0.0779	1.0879
Zn(2)–$O(4)_{ac}$	0.0597	0.2912	−0.0071	−0.0871	0.0799	1.0893
Zn(2)–$O(2)_{ac}$	0.0571	0.2704	−0.0066	−0.0807	0.0742	1.0886
Zn(2)–$O(2)_{ac}$	0.0570	0.2693	−0.0066	−0.0804	0.0739	1.0888
Zn(2)–$O(6)_{ac}$	0.0590	0.2828	−0.0068	−0.0844	0.0775	1.0882
Zn(2)–$O(4)_{ac}$	0.0598	0.2920	−0.0071	−0.0873	0.0801	1.0891
L^2						
$C(1)_{py}$–$N(1)_{py}$	0.3440	−0.9760	−0.4988	−0.7535	0.2548	2.9577
$N(1)_{py}$–$C(5)_{py}$	0.3359	−0.8367	−0.4943	−0.7795	0.2852	2.7336
$C(5)_{py}$–$C(4)_{py}$	0.3166	−0.9148	−0.3305	−0.4323	0.1018	4.2460
$C(4)_{py}$–$C(3)_{py}$	0.3143	−0.9015	−0.3273	−0.4291	0.1019	4.2124
$C(3)_{py}$–$C(2)_{py}$	0.3158	−0.9101	−0.3303	−0.4331	0.1028	4.2136
$C(2)_{py}$–$C(1)_{py}$	0.3192	−0.9314	−0.3359	−0.4390	0.1031	4.2588
$C(1)_{py}$–$N(2)_{azo}$	0.3042	−0.9171	−0.3539	−0.4786	0.1247	3.8392
$N(2)_{azo}$–$N(3)_{azo}$	0.4697	−1.2062	−0.5866	−0.8717	0.2851	3.0578
$N(3)_{azo}$–$C(6)_{ph}$	0.2966	−0.8260	−0.3912	−0.5758	0.1847	3.1181

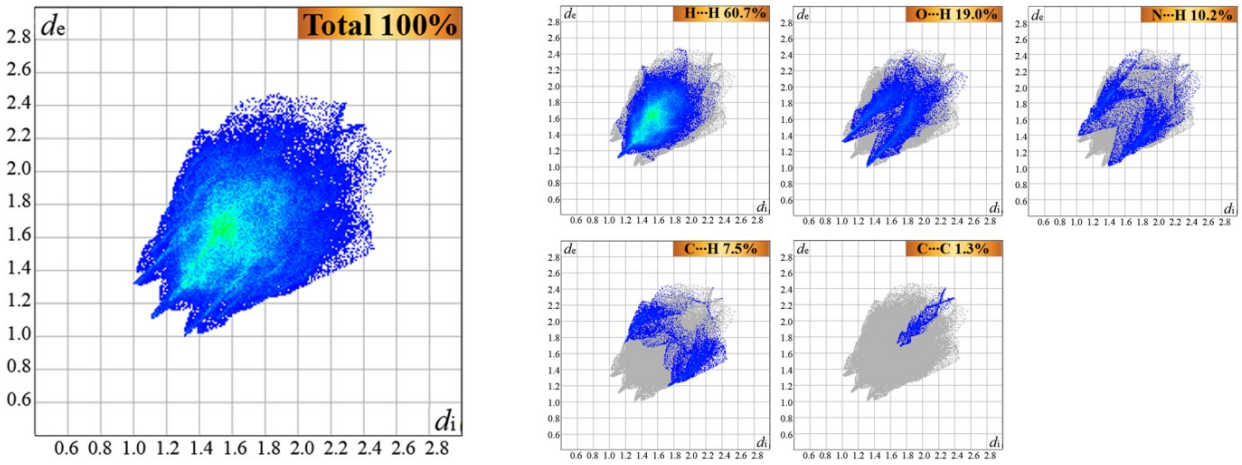

Fig. S3 2D fingerprint plots according to the d_{norm} value for **1**.

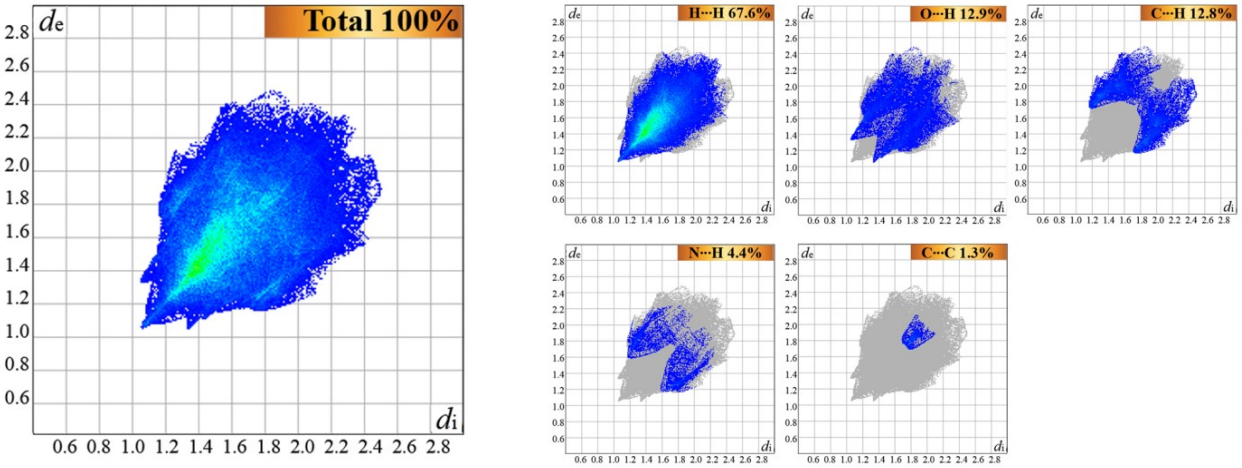

Fig. S4 2D fingerprint plots according to the d_{norm} value for **2**.

Table S11 Energy decomposition analysis based on molecular forcefield (EDA-FF) for complex **1.** All energy is given in kcal mol^{-1}. Δ*E* is calculated at CAM-B3LYP-GD3BJ/6-311G(d,p) level of theory

Dimer	R, Å	Electrostatic	Repulsion	Dispersion	E_{Total}	Δ*E*
D1_1	9.39	–10.63	12.85	–29.60	–27.38	–26.37
D2_1	19.99	0.54	6.99	–23.33	–15.80	–14.77
D3_1	24.64	–3.52	4.75	–15.96	–14.73	–12.31
D4_1	10.65	–4.99	4.78	–7.01	–7.22	–8.64
D5_1	27.24	–0.39	1.87	–9.55	–8.07	–6.45
D6_1	19.44	–2.56	1.89	–5.02	–5.69	–5.37

Table S12 Energy decomposition analysis based on molecular forcefield (EDA-FF) for complex **2**. All energy is given in kcal mol^{-1}. Δ*E* is calculated at CAM-B3LYP-GD3BJ/6-311G(d,p) level of theory

Dimer	R, Å	Electrostatic	Repulsion	Dispersion	E_{Total}	Δ*E*
D1_2	9.81	−9.86	27.57	−73.08	−55.37	−49.00
D2_2	13.98	−16.38	11.05	−17.47	−22.80	−20.61
D3_2	24.11	−2.70	7.83	−20.12	−14.99	−12.81
D4_2	10.53	1.77	6.31	−16.57	−8.48	−9.28
D5_2	20.39	0.01	6.42	−14.00	−7.58	−8.52
D6_2	26.50	−0.03	2.32	−8.81	−6.52	−6.00
D7_2	17.51	0.00	3.62	−9.83	−6.22	−5.98

Table S13 QTAIM analysis of non-covalent interaction in dimer D1_1 of complex **1**

CPs	ρ(r)	$\nabla^2\rho$(r)	*H*(r)	*V*(r)	*G*(r)	*k(r)*	$sign(\lambda_2)\rho$ *	interaction	*E*
1	0.007100	0.021530	0.000481	−0.004421	0.004902	0.9019	−0.7099	O4···H11^{i}	−1.39
2	0.012177	0.044326	0.001617	−0.007847	0.009464	0.8291	−1.2177	O4··· H4^{i}	−2.46
3	0.007466	0.021083	0.000770	−0.003731	0.004501	0.8289	−0.7466	N3^{i} ···H3	−1.17
4	0.010980	0.036439	0.001495	−0.006120	0.007615	0.8037	−0.0109	N2^{i} ···H2	−1.92
5	0.005038	0.015019	0.000779	−0.002196	0.002975	0.7380	−0.5038	Cg1···Cg2	−0.69
6	0.003522	0.010034	0.000390	−0.001728	0.002118	0.8157	−0.3522	H17A···H22B^{i}	−0.54
7	0.006358	0.016104	0.000451	−0.003124	0.003575	0.8738	−0.6358	H15B···H22B^{i}	−0.98
8	0.002937	0.008591	0.000377	−0.001393	0.001771	0.7870	−0.2937	H15B···H20B^{i}	−0.44
9	0.004509	0.011393	0.000322	−0.002205	0.002526	0.8726	−0.4509	H13A···H20B^{i}	−0.69
10	0.002333	0.007028	0.000359	−0.001039	0.001398	0.7434	−0.2333	H13A···H18B^{i}	−0.33
11	0.003634	0.009616	0.000328	−0.001747	0.002075	0.8417	−0.3634	H11B···H18B^{i}	−0.55
12	0.002076	0.006516	0.000000	−0.000907	0.001268	0.7151	−0.2076	H11B···H16A^{i}	−0.28
13	0.002713	0.007290	0.000344	−0.001134	0.001478	0.7672	−0.2713	*C*g1···H16A^{i}	−0.36
14	0.004593	0.012114	0.000465	−0.002098	0.002563	0.8185	−0.4593	*C*g1···H14B^{i}	−0.66

*Values of $sign(\lambda_2)\rho$ are multiple by 10^{-2}; Half of the data were presented due to symmetry consideration

Table S14 QTAIM analysis of non-covalent interaction in dimer D2_1 of complex **1**

CPs	ρ(r)	$\nabla^2\rho$(r)	H(r)	V(r)	G(r)	$k(r)$	$sign(\lambda_2)\rho^*$	interaction	E
1	0.006723	0.018535	0.000570	−0.003494	0.004064	0.8598	−0.6723	N2^{ii} ···H22C	−1.10
2	0.002005	0.007187	0.000360	−0.001077	0.001437	0.7496	−0.2005	N3^{ii} ···H20A	−0.34
3	0.003122	0.008957	0.000410	−0.001420	0.001830	0.7762	−0.3122	*Cg*1^{ii} ···H20A	−0.45
4	0.003529	0.010210	0.000459	−0.001634	0.002093	0.7805	−0.3529	*Cg*1^{ii} ···H19A	−0.51
5	0.004397	0.011793	0.000456	−0.002037	0.002493	0.8172	−0.4397	*Cg*1^{ii} ···H18A	−0.64
6	0.002337	0.007929	0.000438	−0.001107	0.001545	0.7167	−0.2337	*Cg*1^{ii} ···H17A	−0.35
7	0.002891	0.009273	0.000413	−0.001492	0.001905	0.7830	−0.2891	H16B···H11B^{ii}	−0.47
8	0.003443	0.010351	0.000404	−0.001779	0.002184	0.8149	−0.3443	H15B···H12A^{ii}	−0.56
9	0.003298	0.010590	0.000448	−0.001752	0.002200	0.7965	−0.3298	H14A···H12A^{ii}	−0.55
10	0.002780	0.008821	0.000395	−0.001415	0.001810	0.7818	−0.2780	H14···H13^{ii}	−0.44

*Values of $sign(\lambda_2)\rho$ are multiple by 10^{-2}; Half of the data were presented due to symmetry consideration

Table S15 QTAIM analysis of non-covalent interaction in dimer D3_1 of complex **1**

CPs	ρ(r)	$\nabla^2\rho$(r)	H(r)	V(r)	G(r)	$k(r)$	$sign(\lambda_2)\rho^*$	interaction	E
1	0.005411	0.016618	0.000532	−0.003090	0.003622	0.8530	−0.5411	O2^{iii} ···H22A	−0.97
2	0.005708	0.017309	0.000703	−0.002922	0.003625	0.8062	−0.5708	H21A···H9^{iii}	−0.92
3	0.001012	0.003576	0.000256	−0.000382	0.000638	0.5982	−0.1012	H19B···H11B^{iii}	−0.12
4	0.001237	0.004212	0.000284	−0.000485	0.000769	0.6304	−0.1237	H17B···HA^{iii}	−0.15
5	0.001256	0.004272	0.000285	−0.000497	0.000783	0.6353	−0.1256	H15A···HA^{iii}	−0.16

*Values of $sign(\lambda_2)\rho$ are multiple by 10^{-2}; Half of the data were presented due to symmetry consideration

Table S16 QTAIM analysis of non-covalent interaction in dimer D4_1 of complex **1**

CPs	ρ(r)	$\nabla^2\rho$(r)	H(r)	V(r)	G(r)	$k(r)$	$sign(\lambda_2)\rho^*$	interaction	E
1	0.011046	0.038090	0.001386	−0.006750	0.008136	0.8296	−1.1046	O3^{iv}···H7	−2.12

*Values of $sign(\lambda_2)\rho$ are multiple by 10^{-2}; Half of the data were presented due to symmetry consideration

Table S17 QTAIM analysis of non-covalent interaction in dimer D5_1 of complex **1**

CPs	ρ(r)	$\nabla^2\rho$(r)	H(r)	V(r)	G(r)	$k(r)$	$sign(\lambda_2)\rho^*$	interaction	E
1	0.002380	0.009215	0.000509	−0.001286	0.001795	0.7165	−0.2380	O1^{v}···H22C	−0.41
2	0.002143	0.007340	0.000439	−0.000957	0.001396	0.6855	−0.2143	H22C···H12B^{v}	−0.30
3	0.002337	0.007904	0.000460	−0.001056	0.001516	0.6967	−0.2337	H20B···H12^{v}	−0.33
4	0.001926	0.006502	0.000388	−0.000850	0.001238	0.6867	−0.1926	H20B···H14B^{v}	−0.27
5	0.001792	0.006081	0.000371	−0.000778	0.001149	0.6768	−0.1792	H18B···H16A^{v}	−0.24

*Values of $sign(\lambda_2)\rho$ are multiple by 10^{-2}; Half of the data were presented due to symmetry consideration

Table S18 QTAIM analysis of non-covalent interaction in dimer D6_1 of complex **1**

CPs	ρ(r)	$\nabla^2\rho$(r)	H(r)	V(r)	G(r)	$k(r)(r)$	$sign(\lambda_2)\rho^*$	interaction	E
1	0.006858	0.022006	0.000703	−0.004095	0.004798	0.8534	−0.6858	O3^{vi}···H19A	−1.28

*Values of $sign(\lambda_2)\rho$ are multiple by 10^{-2}; Half of the data were presented due to symmetry consideration

Table S19 QTAIM analysis of non-covalent interaction in dimer D1_2 of complex **2**

CPs	ρ(r)	$\nabla^2\rho$(r)	H(r)	V(r)	G(r)	$k(r$	$sign(\lambda_2)\rho^*$	interaction	E
1	0.002339	0.007204	0.000355	−0.001090	0.001446	0.7541	−0.2340	H23C···H17A^{i}	−0.34
2	0.002231	0.007672	0.000396	−0.001127	0.001522	0.7402	−0.2231	H22C···H15A^{i}	−0.35
3	0.002988	0.009242	0.000390	−0.001531	0.001921	0.7969	−0.2988	H22B···H16A^{i}	−0.48
4	0.003632	0.010757	0.000402	−0.001885	0.002287	0.8241	−0.3632	H22B···H14A^{i}	−0.59
5	0.002947	0.010411	0.000496	−0.001611	0.002107	0.7648	−0.2947	H22B···H15A^{i}	−0.51
6	0.003353	0.010003	0.000391	−0.001719	0.002110	0.8147	−0.3353	H21B···H15A^{i}	−0.54
7	0.003557	0.010825	0.000423	−0.001860	0.002283	0.8148	−0.3557	H21B···H13B^{i}	−0.58
8	0.004431	0.012618	0.000419	−0.002317	0.002736	0.8470	−0.4431	H20A···H14A^{i}	−0.73
9	0.003558	0.012963	0.000601	−0.002038	0.002639	0.7722	−0.3558	H20A···H13B^{i}	−0.64
10	0.005033	0.014587	0.000489	−0.002670	0.003158	0.8453	−0.5033	H20A···H12A^{i}	−0.84
11	0.004090	0.012232	0.000446	−0.002166	0.002612	0.8292	−0.4090	H19A···H13B^{i}	−0.68
12	0.004950	0.013946	0.000431	−0.002626	0.003056	0.8591	−0.4950	H18B···H12A^{i}	−0.82
13	0.003220	0.011947	0.000515	−0.001958	0.002472	0.7919	−0.3212	O7^{i}···H19A	−0.61
14	0.006117	0.017832	0.000458	−0.003542	0.004000	0.8856	−0.6117	O5^{i}···H14B	−1.11
15	0.006143	0.019799	0.000635	−0.003680	0.004315	0.8529	−0.6143	O5^{i}···H25B^{ii}	−1.15
16	0.004006	0.010622	0.000403	−0.001850	0.002253	0.8212	−0.4006	*C*g2^{i}···H18B	−0.58
17	0.004928	0.012660	0.000457	−0.002251	0.002708	0.8312	−0.4928	*C*g2^{i}···H17B	−0.71
18	0.005399	0.014307	0.000497	−0.002583	0.003080	0.8386	−0.5399	*C*g2^{i}···H16B	−0.81
19	0.004552	0.012346	0.000486	−0.002115	0.002601	0.8132	−0.4552	*C*g2^{i}···H15B	−0.66
20	0.004075	0.009773	0.000391	−0.001661	0.002052	0.8093	−0.4075	*C*g1^{i}···*C*g2^{i}	−0.52

*Values of $sign(\lambda_2)\rho$ are multiple by 10^{-2}; Half of the data were presented due to symmetry consideration

Table S20 QTAIM analysis of non-covalent interaction in dimer D2_2 of complex **2**

CPs	ρ(r)	$\nabla^2\rho$(r)	H(r)	V(r)	G(r)	$k(r)$	$sign(\lambda_2)\rho^*$	interaction	E
1	0.011341	0.043978	0.001769	−0.007456	0.009225	0.8082	−1.1341	O3^{iii}···H4	−2.34
2	0.007811	0.028860	0.001085	−0.005046	0.006130	0.8231	−0.7811	O3^{iii}···H3	−1.58
3	0.002611	0.010593	0.000610	−0.001428	0.002038	0.7007	−0.2611	*C*g1···*C*g3^{iii}	−0.45
4	0.005306	0.015158	0.000701	−0.002388	0.003089	0.7731	−0.5306	*C*g1···*C*g1	−0.75
5	0.005304	0.015150	0.000700	−0.002387	0.003087	0.7732	−0.5304	*C*g1···*C*g1	−0.75

*Values of $sign(\lambda_2)\rho$ are multiple by 10^{-2}; Half of the data were presented due to symmetry consideration

Table S21 QTAIM analysis of non-covalent interaction in dimer D3_2 of complex **2**

CPs	ρ(r)	$\nabla^2\rho$(r)	H(r)	V(r)	G(r)	$k(r)$	$sign(\lambda_2)\rho^*$	interaction	E
1	0.004923	0.016326	0.000566	−0.002950	0.003516	0.8391	−0.4924	O6^{iv}···H23B	−0.93
2	0.000739	0.002886	0.000229	−0.000264	0.000493	0.5355	−0.0740	O3^{v} ···H23A	−0.08
3	0.005999	0.018606	0.000773	−0.003106	0.003879	0.8008	−0.5999	H23B···H29A^{iv}	−0.97
4	0.005378	0.017729	0.000759	−0.002915	0.003674	0.7935	−0.5378	H23A···H25C^{v}	−0.91
5	0.006301	0.018545	0.000660	−0.003317	0.003977	0.8341	−0.6301	H22A···H25C^{v}	−1.04
6	0.002373	0.007741	0.000406	−0.001124	0.001529	0.7346	−0.2373	H22A···H10A^{iv}	−0.35
7	0.003721	0.009804	0.000328	−0.001796	0.002124	0.8458	−0.3721	H22A···H12A^{iv}	−0.56
8	0.003186	0.008571	0.000320	−0.001503	0.001823	0.8244	−0.3186	H20B···H14A^{iv}	−0.47
9	0.002796	0.007793	0.000327	−0.001295	0.001621	0.7984	−0.2796	H18A···H16A^{iv}	−0.41
10	0.001500	0.004924	0.000318	−0.000594	0.000913	0.6512	−0.1500	H16A···H16A^{iv}	−0.19

*Values of $sign(\lambda_2)\rho$ are multiple by 10^{-2}; Half of the data were presented due to symmetry consideration

Table S22 QTAIM analysis of non-covalent interaction in dimer D4_2 of complex **2**

CPs	ρ(r)	$\nabla^2\rho$(r)	H(r)	V(r)	G(r)	$k(r)$	$sign(\lambda_2)\rho^*$	interaction	E
1	0.005262	0.017401	0.000764	−0.002823	0.003586	0.7871	−0.5262	N2^{vii}···H27A	−0.89
2	0.004922	0.015563	0.000727	−0.002438	0.003164	0.7704	−0.4922	*Cg*2^{vii}···H27C	−0.76
3	0.008249	0.025575	0.000782	−0.004829	0.005611	0.8606	−0.8249	O3^{vii}···H27A	−1.52

*Values of $sign(\lambda_2)\rho$ are multiple by 10^{-2}; Half of the data were presented due to symmetry consideration

Table S23 QTAIM analysis of non-covalent interaction in dimer D5_2 of complex **2**

CPs	ρ(r)	$\nabla^2\rho$(r)	H(r)	V(r)	G(r)	$k(r)$	$sign(\lambda_2)\rho^*$	interaction	E
1	0.001461	0.004922	0.000309	−0.000612	0.000922	0.6646	−0.1461	H13···H13B^{vi}	−0.19
2	0.007652	0.021456	0.000777	−0.003809	0.004587	0.8305	−0.7652	H21A···H2^{vi}	−1.20
3	0.004526	0.013694	0.000543	−0.002338	0.002881	0.8117	−0.4526	H17A···H7^{vi}	−0.73
4	0.003685	0.012229	0.000567	−0.001923	0.002490	0.7723	−0.3685	H17A···H8^{vi}	−0.60
5	0.007906	0.021140	0.000722	−0.003840	0.004563	0.8417	−0.7906	H15A···H8^{vi}	−1.20
6	0.002288	0.007192	0.000369	−0.001059	0.001429	0.7415	−0.2288	H23A···H3^{vi}	−0.33

*Values of $sign(\lambda_2)\rho$ are multiple by 10^{-2}; Half of the data were presented due to symmetry consideration

Table S24 QTAIM analysis of non-covalent interaction in dimer D6_2 of complex **2**

CPs	ρ(r)	$\nabla^2\rho$(r)	H(r)	V(r)	G(r)	$k(r)$	$sign(\lambda_2)\rho$*	interaction	E
1	0.005752	0.018175	0.000779	−0.002986	0.003765	0.7931	−0.5752	H29C···H19B^{viii}	−0.94
2	0.004422	0.013302	0.000528	−0.002270	0.002798	0.8114	−0.4422	H29B···H20B^{viii}	−0.71
3	0.004272	0.013477	0.000585	−0.002199	0.002784	0.7899	−0.4272	H29B···H18A^{vii} ^{i}	−0.69
4	0.002267	0.007645	0.000400	−0.001111	0.001511	0.7353	−0.2267	H29A···H17^{viii}	−0.35

*Values of $sign(\lambda_2)\rho$ are multiple by 10^{-2}; Half of the data were presented due to symmetry consideration

Table S25 QTAIM analysis of non-covalent interaction in dimer D7_2 of complex **2**

CPs	ρ(r)	$\nabla^2\rho$(r)	H(r)	V(r)	G(r)	$k(r)$	$sign(\lambda_2)\rho^*$	interaction	E
1	0.006117	0.017273	0.000644	−0.003031	0.003675	0.8248	−0.6116	H23C···H8^{ix}	−0.95
2	0.001706	0.006695	0.000426	−0.000821	0.001248	0.6583	−0.1706	O7^{ix} ···H21B	−0.26
3	0.003132	0.009208	0.000401	−0.001500	0.001901	0.7889	−0.3132	H19A···H13A^{ix}	−0.47
4	0.002752	0.008088	0.000370	−0.001283	0.001652	0.7762	−0.2752	H17B···H15B^{ix}	−0.40

*Values of $sign(\lambda_2)\rho$ are multiple by 10^{-2}; Half of the data were presented due to symmetry consideration