SUPPORTING INFORMATION

Table S1. Crystallographic data and refinement parameters for crystals **1**–**6**

Parameter	**1** · $2H_2O$	**2** · $2H_2O$	**3** · $2CH_3CN$	**4**	**5** · $2CH_3CN$	**6** · $0.5H_2O$
Empirical formula	$C_{30}H_{55}B_{20}N_9O_2$	$C_{24}H_{34}B_{12}N_4O_2$	$C_{20}H_{42}B_{10}N_6$	$C_{24}H_{28}B_{10}N_4$	$C_{60}H_{80}B_{12}N_6O_6$	$C_{54}H_{48.5}B_{10}N_9O_{0.5}$
Fw	790.30	540.27	474.69	480.60	1111.02	940.62
Crystal system, space group	Triclinic, $P\bar{1}$	Monoclinic, $P2_1/m$	Orthorhombic, $Pna2_1$	Monoclinic, $P2_1/n$	Monoclinic, $C2/c$	Orthorhombic, $P2_12_12$
T (K)	173(2)	120.0(2)	173.0(2)	100.0(2)	120.0(2)	100.0(2)
a (Å)	7.437(4)	7.9096(3)	15.893(2)	20.430(16)	24.465(3)	16.586(2)
b (Å)	17.777(10)	18.9027(6)	8.7035(13)	8.611(7)	14.7934(17)	25.190(3)
c (Å)	17.866(9)	9.8240(4)	20.298(3)	30.41(2)	17.787(2)	11.5646(14)
α (°)	115.710(8)	90	90	90	90	90
β (°)	90.072(9)	108.169(1)	90	109.200(14)	108.284(2)	90
γ (°)	93.744(9)	90	90	90	90	90
V ($Å^3$)	2123(2)	1395.58(9)	2807.8(7)	5052(7)	6112.5(12)	4831.7(10)
Z	2	2	4	8	4	4
μ (cm^{-1})	0.071	0.570	0.063	0.069	0.074	0.075
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14362, 6680, 2714	15786, 2451, 2115	10279, 5122, 2876	21203, 5884, 3247	39755, 9349, 6367	28518, 7690, 4297
R_{int}	0.0879	0.0607	0.0523	0.1258	0.0691	0.1072
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.0873, 0.2000, 1.046	0.0848, 0.1765, 1.009	0.0548, 0.1371, 1.008	0.0541, 0.1175, 0.962	0.0576, 0.1654, 1.014	0.1149, 0.2505, 1.133
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e $Å^{-3}$)	0.45, –0.30	0.64, –0.24	0.23, –0.20	0.20, –0.23	0.61, –0.35	0.82, -0.32

Table S2. Maxima of selected absorption bands in IR spectra of compounds **1–6** as compared to alkali metal *closo*-borates (cm^{-1}).

	ν(NH)	**ν(BH)**	**ν(CN), ν(CC) heterocycle**	**π(CH) heterocycle**
$K_2[B_{10}H_{10}]$	—	2529, 2461	—	—
Phen	—	—	1586	854, 739
4	3095	2510, 2477, 2451, 2421	1658, 1631, 1616, 1595	855, 844, 719, 715
6 · 0.5H2O	3164, 3152	2495, 2476, 2414	1656, 1651, 1618, 1610, 1543	824, 761
BPA	3255, 3181, 3102	—	1599, 1566, 1531	769,735
1 · $2H_2O$	3286, 3236, 3204, 3136	2543, 2492, 2444, 2420	1641, 1591, 1528	787, 781, 773
3 · $2CH_3CN$	3467, 3316, 3255, 3212, 3145, 3111	2499, 2466, 2448, 2404	1648, 1612	773, 721
$Cs_2[B_{12}H_{12}]$	—	2465	—	—
5 · CH_3CN	3410, 3361	2484, 2461, 2447, 2422	1648, 1607, 1549, 1531, 1500	847, 812, 785
2 · $2H_2O$	3098, 3063	2487, 2443	1629, 1608, 1586	851, 783, 738, 719

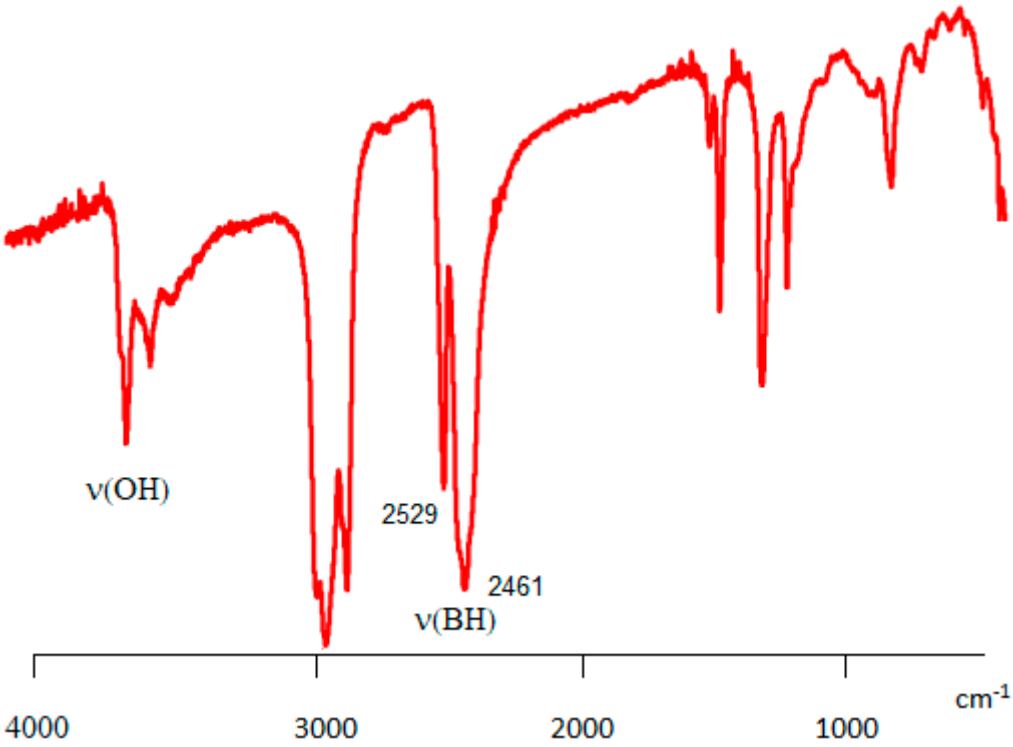

Fig. S1. IR spectrum of $K_2[B_{10}H_{10}]\cdot nH_2O$ (Nujol mull).

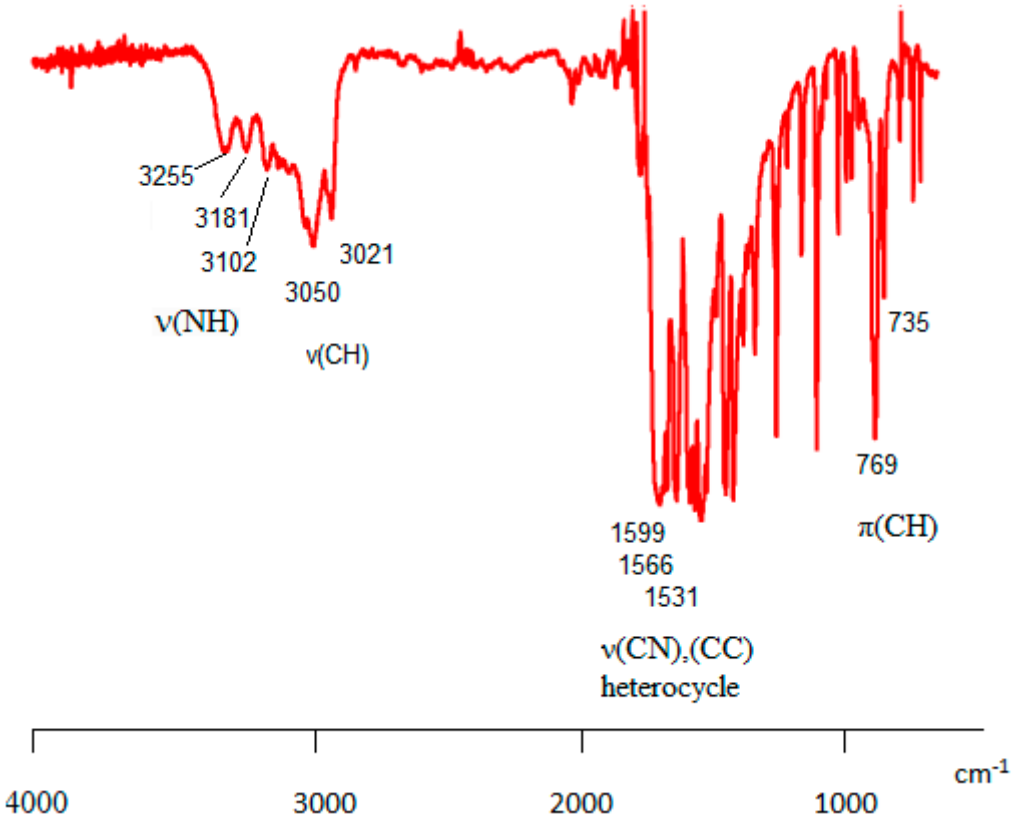

Fig. S2. IR spectrum of bpa (thin layer).

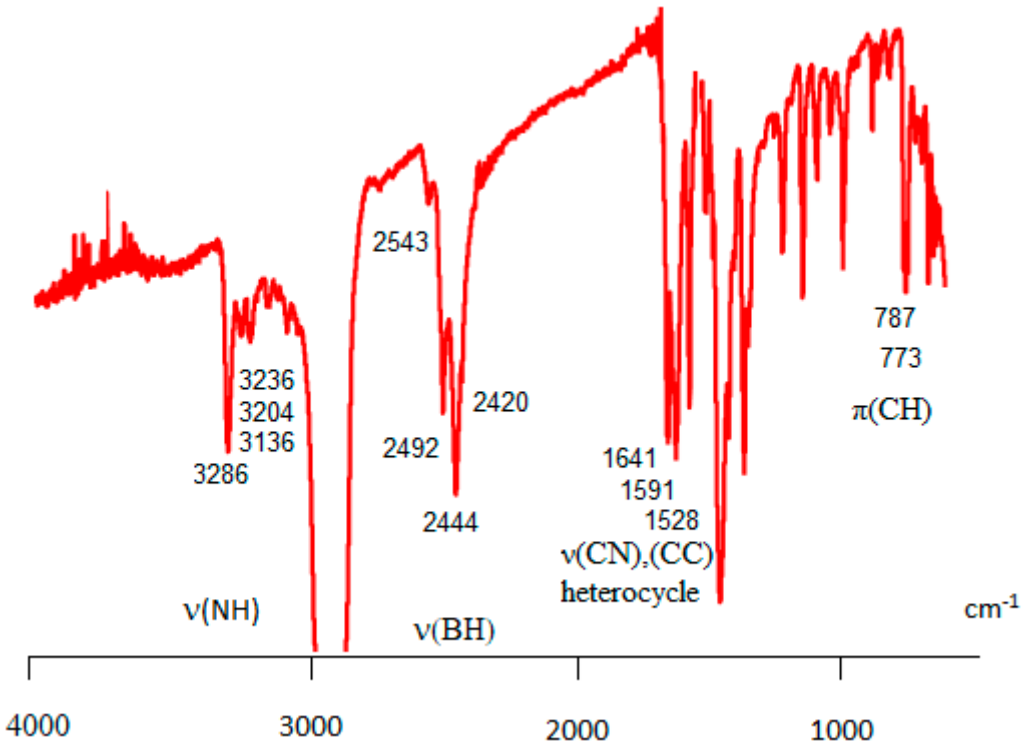

Fig. S3. IR spectrum of $(Hbpa)_2(H_2bpa)[B_{10}H_{10}]_2$ (**1** · $2H_2O$) (Nujol mull).

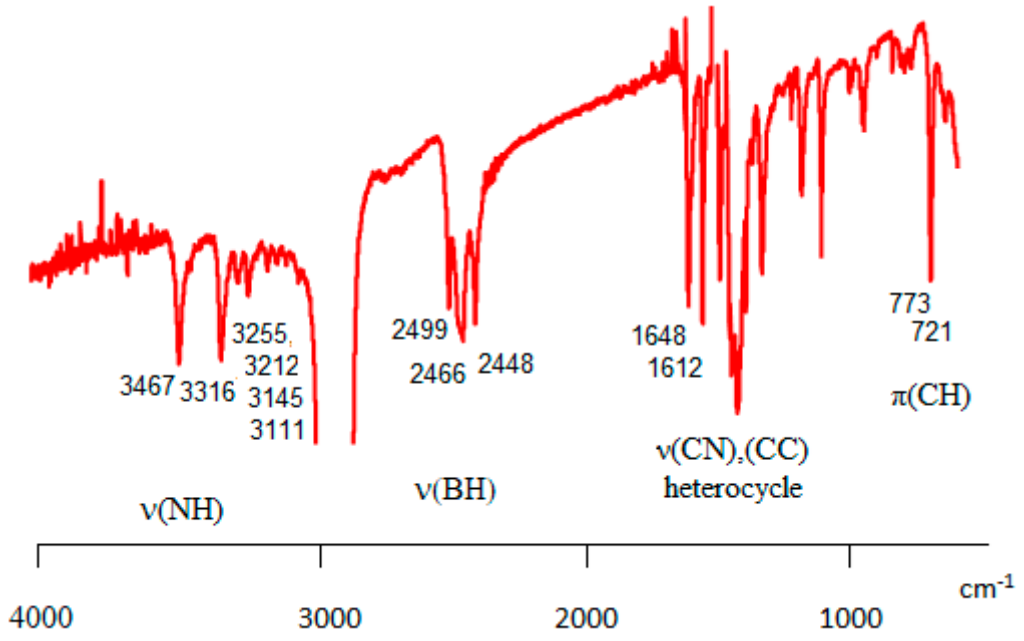

Fig. S4. IR spectrum of $(NHEt_3)(Hbpa)[B_{10}H_{10}]$ (**3** · $2CH_3CN$) (Nujol mull).

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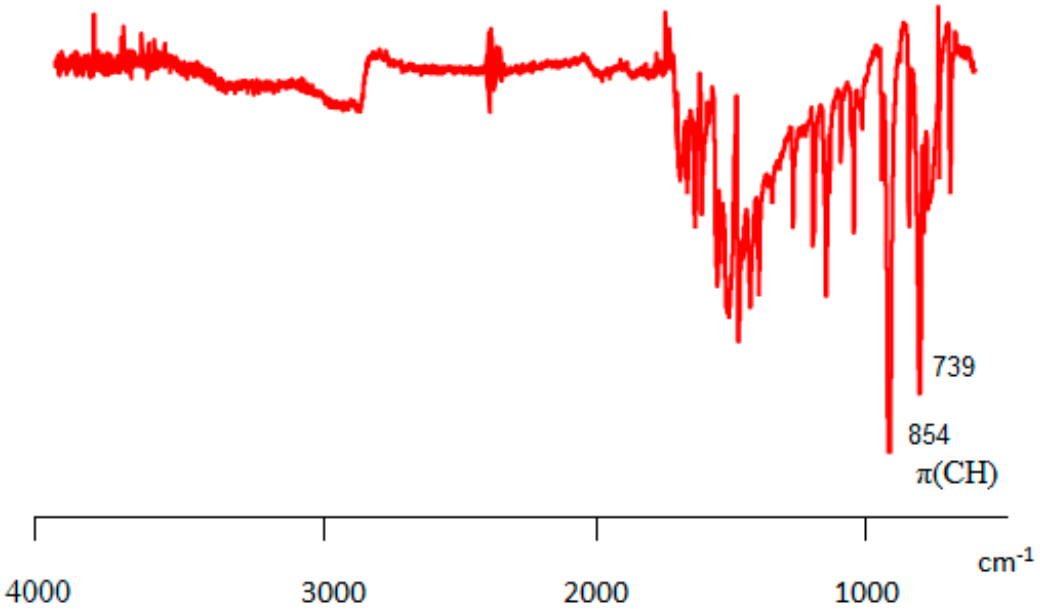


Fig. S5. IR spectrum of phen (thin layer).

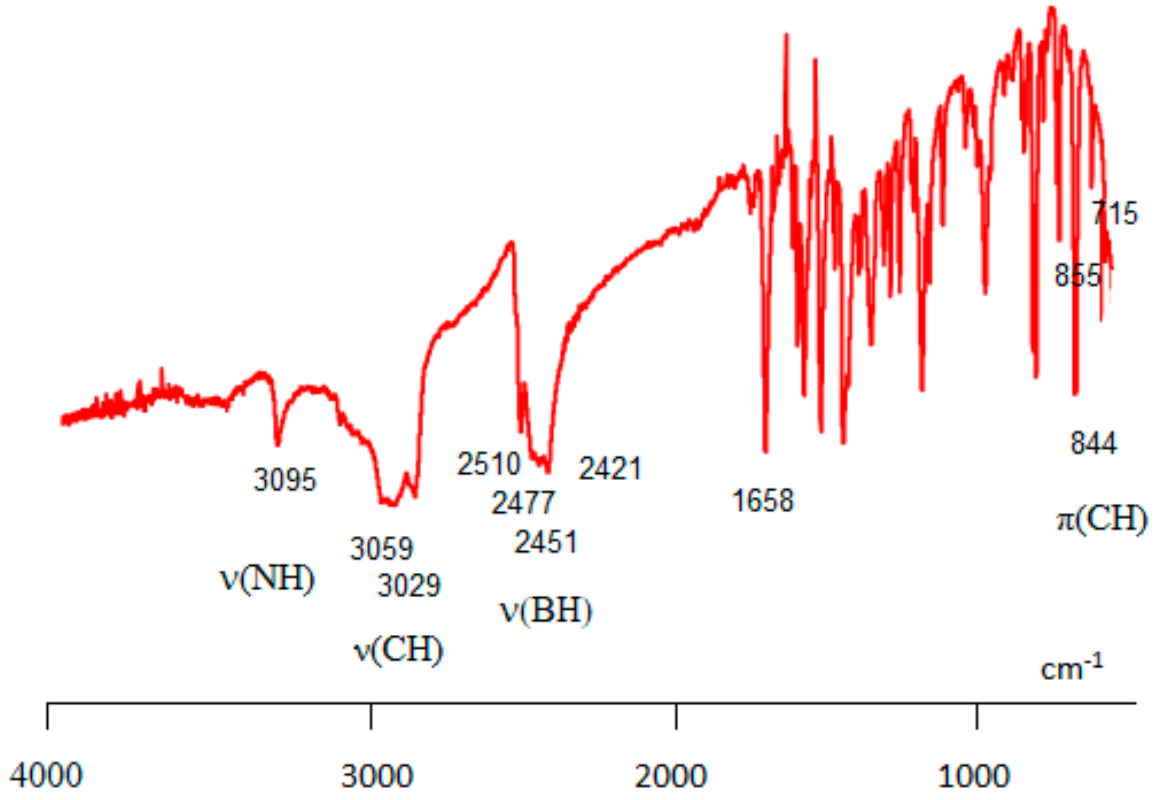


Fig. S6. IR spectrum of $[Hphen)]_2[B_{10}H_{10}]$ (**4**) (thin layer).

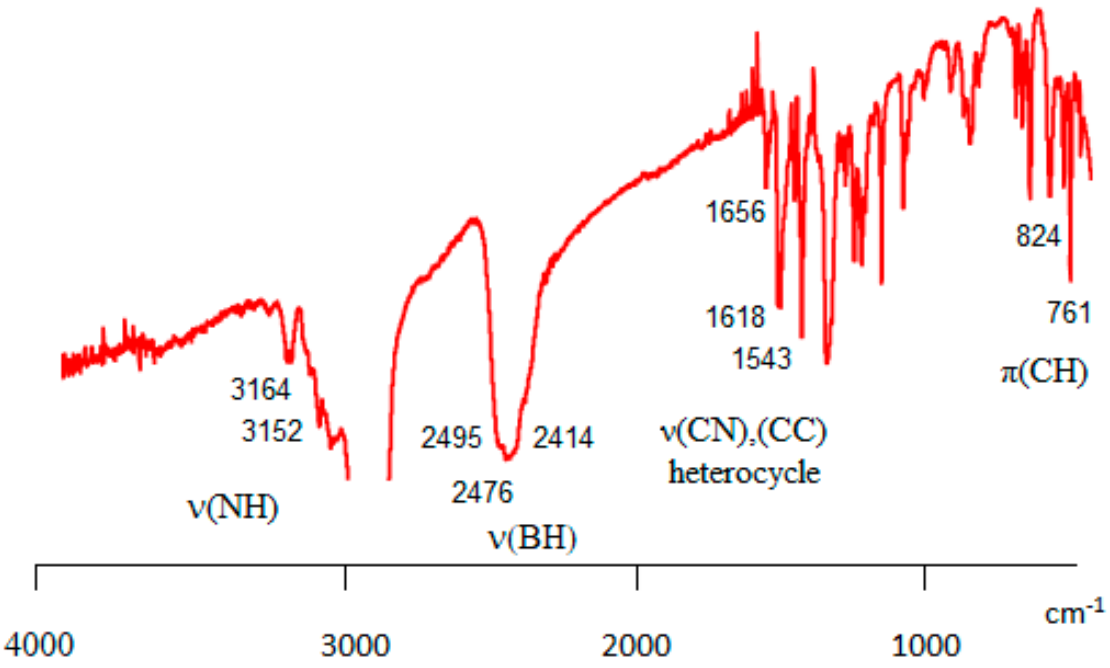


Fig. S7. IR spectrum of $[Hphen]_2(phen)_{2.5}][B_{10}H_{10}]$ (**6** · $0.5H_2O$) (Nujol mull).

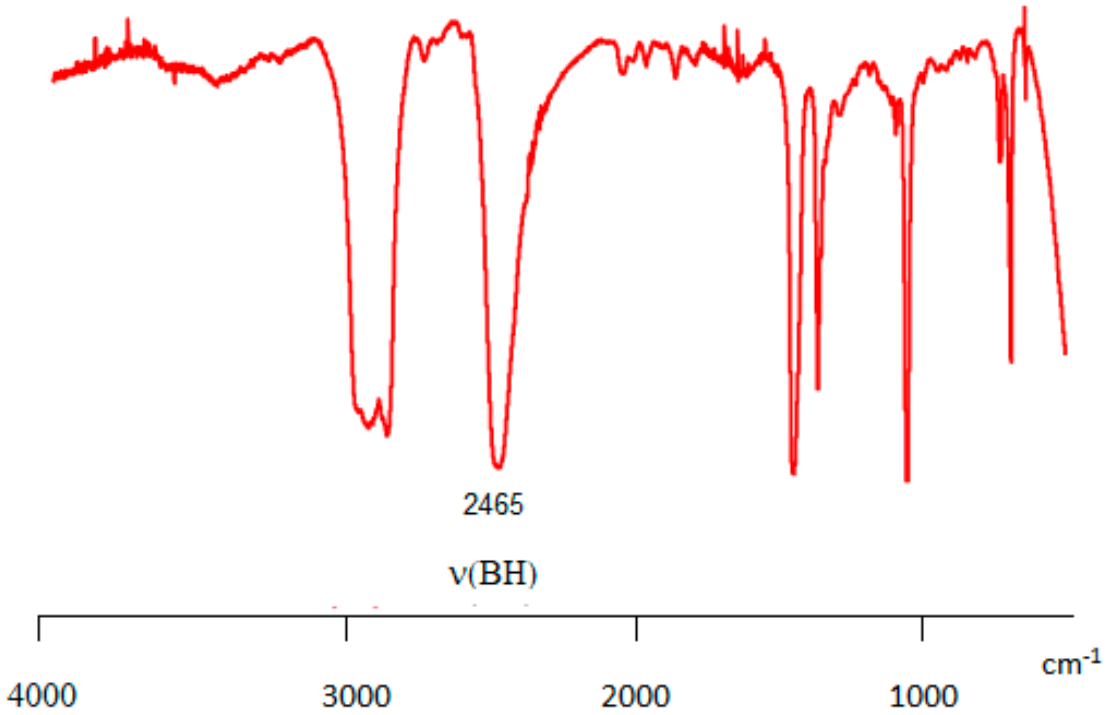


Fig. S8. IR spectrum of $Cs_2[B_{12}H_{12}]$ (Nujol mull).

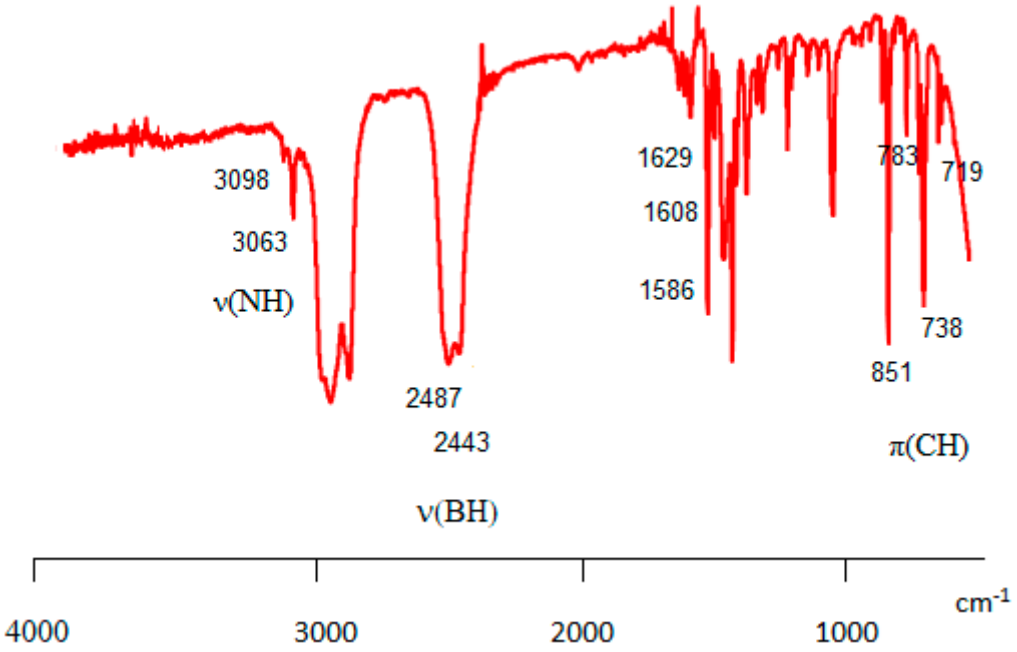


Fig. S9. IR spectrum of $[PhenH]_2[B_{12}H_{12}]$ (**2** · $2H_2O$) (Nujol mull).

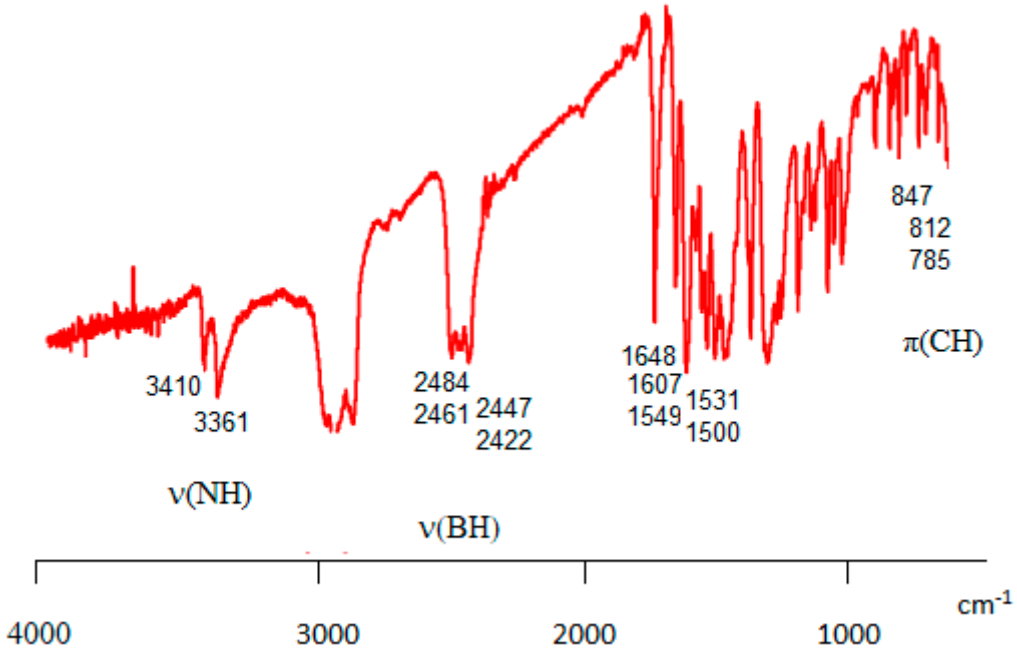
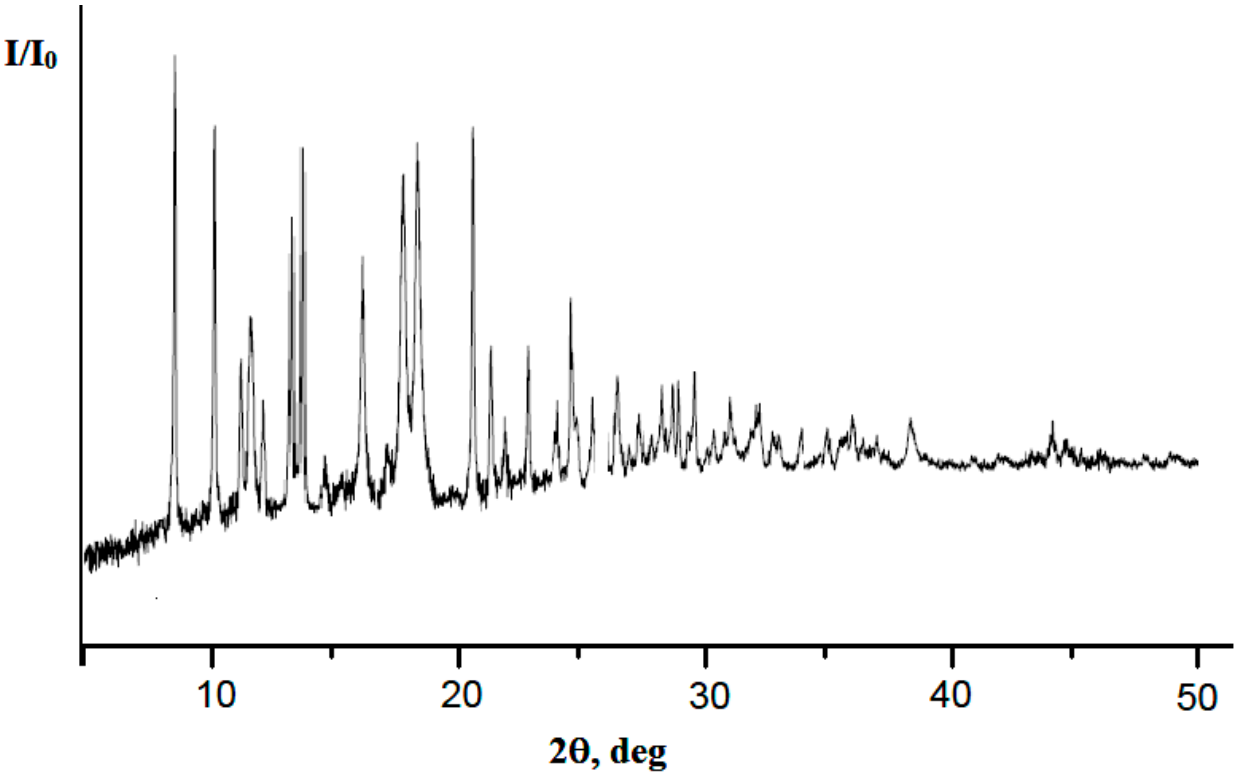


Fig. S10. IR spectrum of $[Rh6GH]_2[B_{12}H_{12}]$ · CH_3CN (**5** · CH_3CN) (Nujol mull).

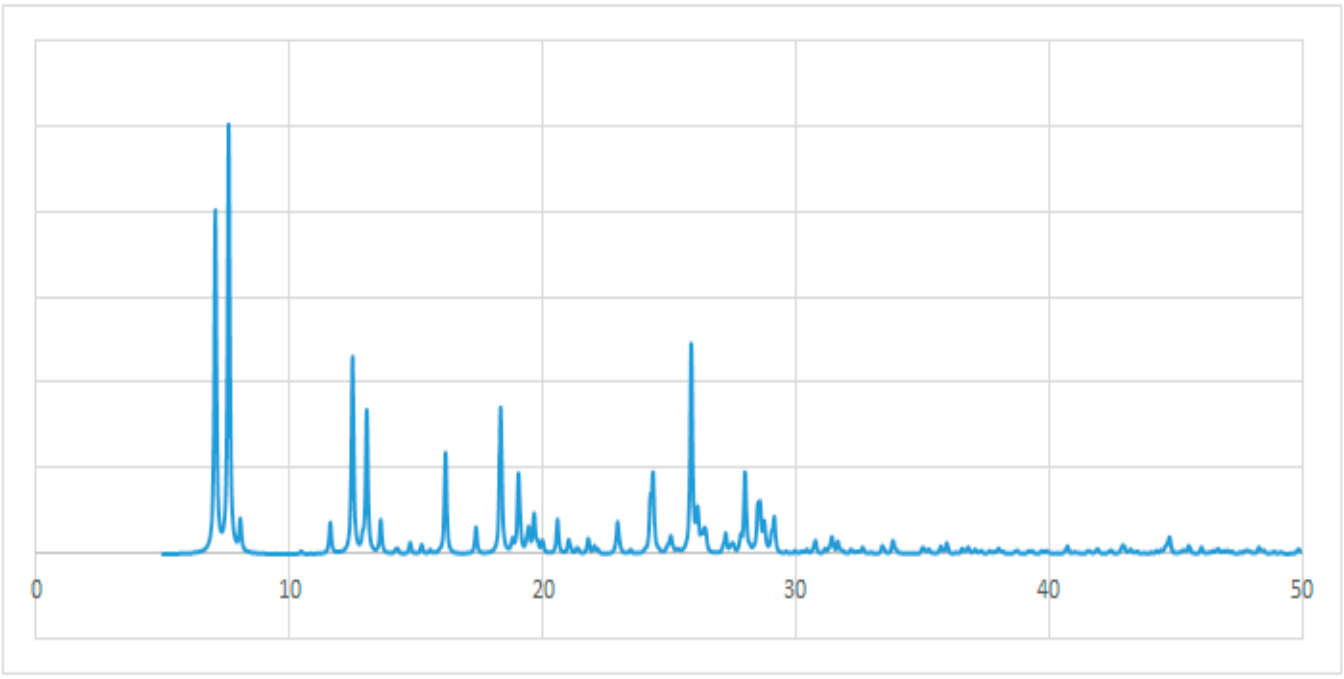
(a)



(b)

Fig. S11. (a) Experimental and (b) calculated X-ray diffraction patterns of $[PhenH)]_2[B_{10}H_{10}]$ (**4**).

a)



b)

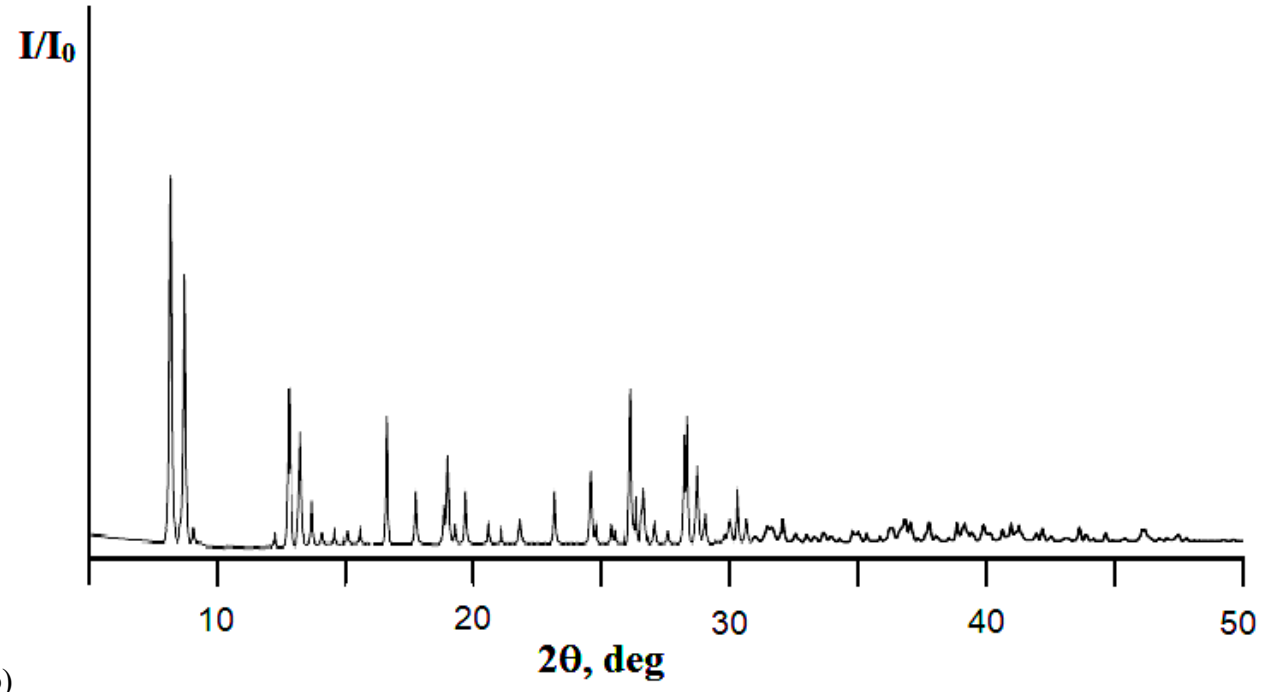


Fig. S12. (a) Experimental and (b) calculated X-ray diffraction patterns of $[Rh6GH]_2[B_{12}H_{12}] \cdot 2CH_3CN$ (**5** · $2CH_3CN$).

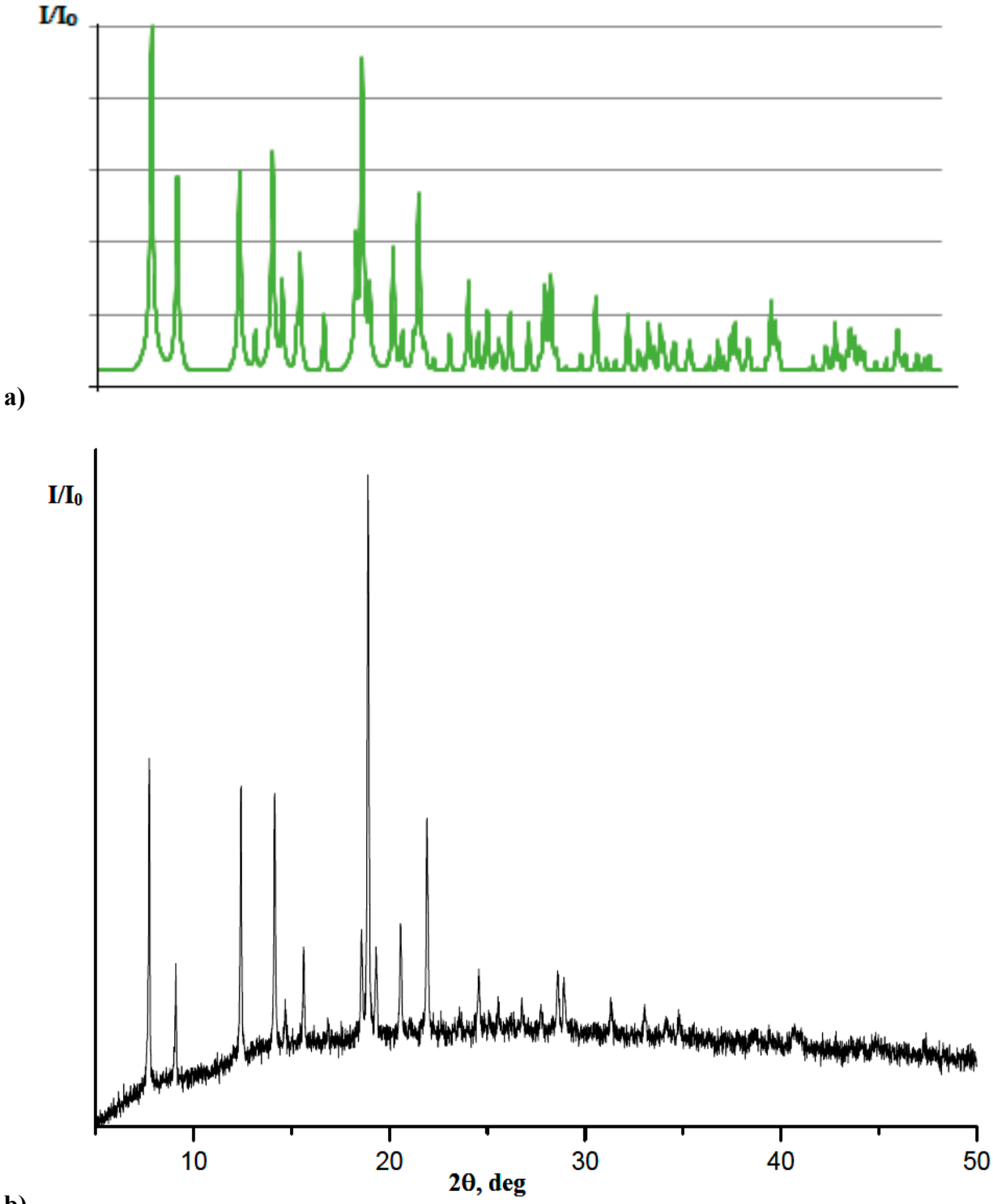


Fig. S13. (a) Experimental and (b) calculated (from ref. [36]) X-ray diffraction patterns of complex $[Co(Phen)_3][B_{10}H_{10}]$ (**7**).