Electronic Supplementary Material (ESI) for Dalton Transactions

Coumarin-based "turn-on" fluorescent sensor for determination of Al^{3+}: Single crystal X-ray structure and cell staining properties

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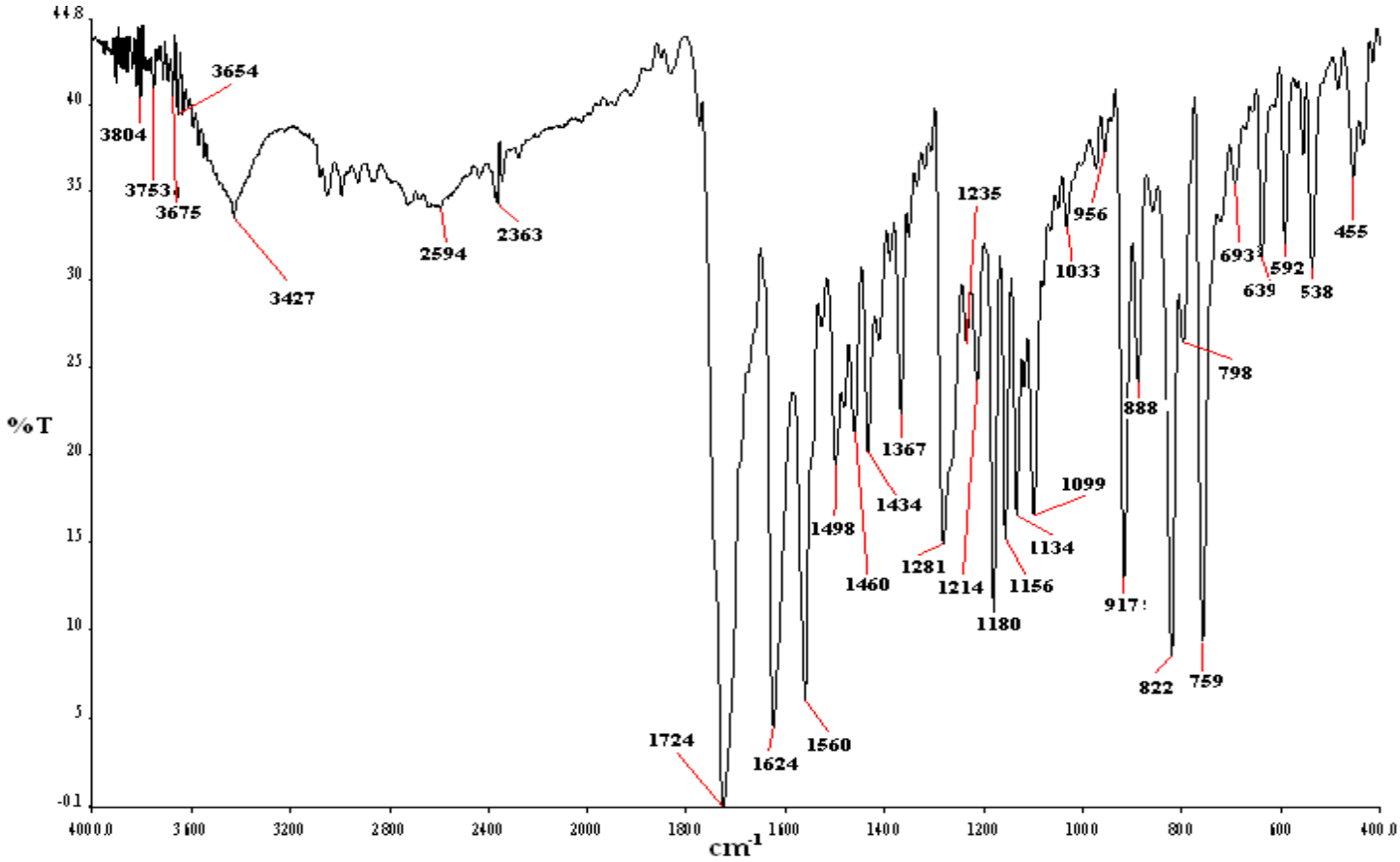


Fig. S1 FTIR spectrum of **HBC**.

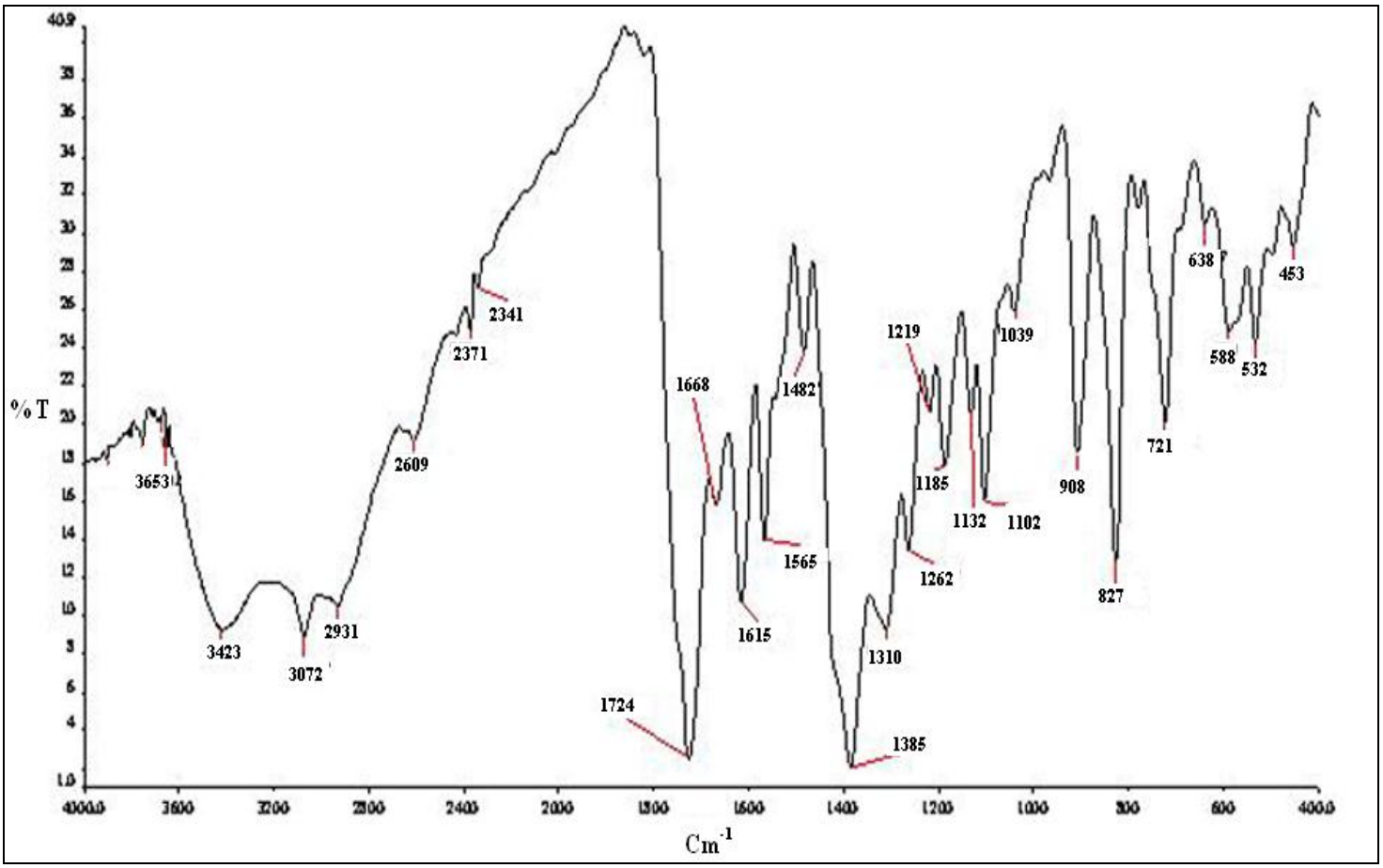


Fig. S2 FTIR spectrum of **[Al(HBC)(MeOH)(NO_3)$_3$]**.

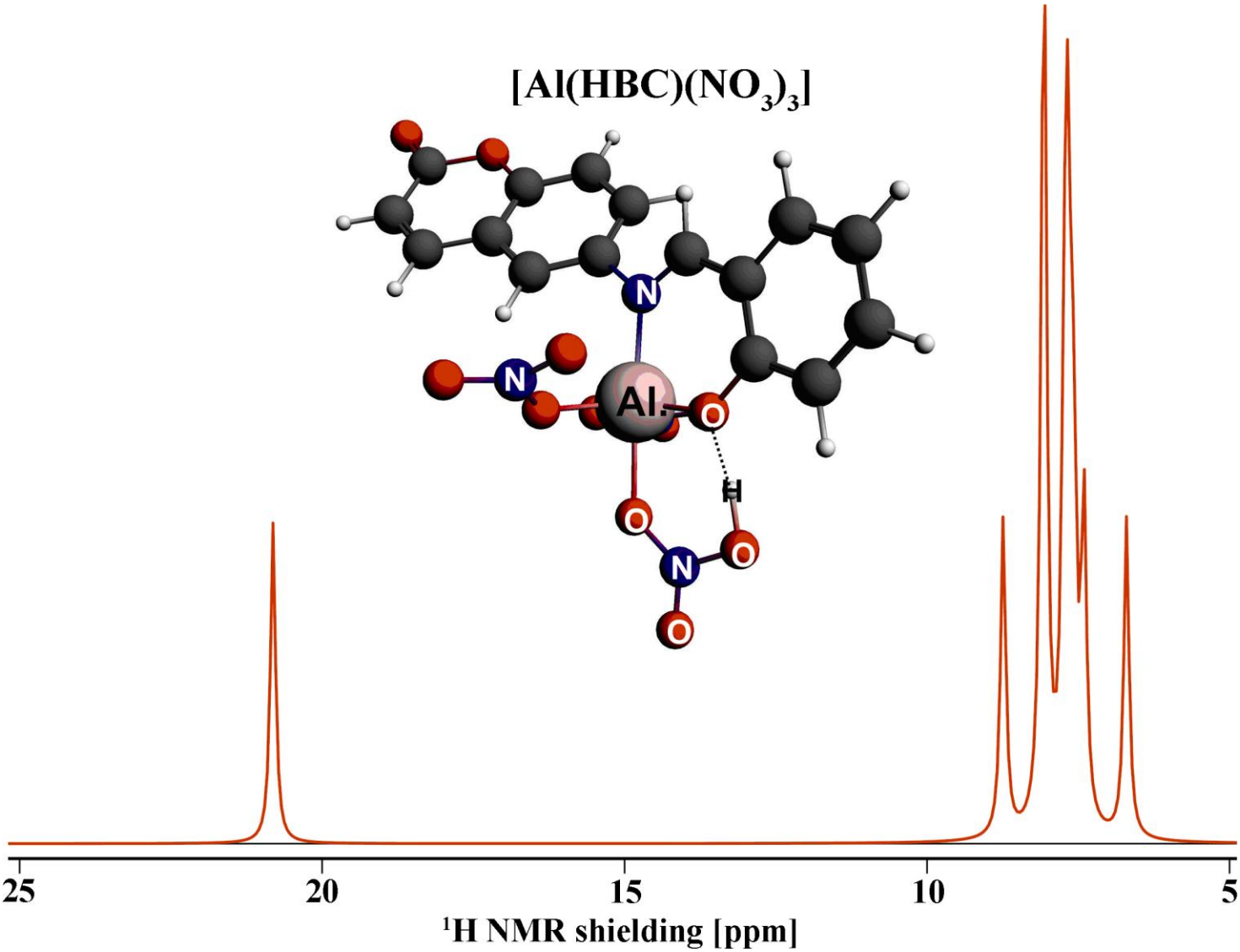


Fig. S3 DFT optimized structure of **[Al(HBC)(NO$_3$)$_3$]** together with the calculated ^{1}H NMR spectrum based on GIAO approach as implemented in the ADF program. Values are provided with respect to TMS.

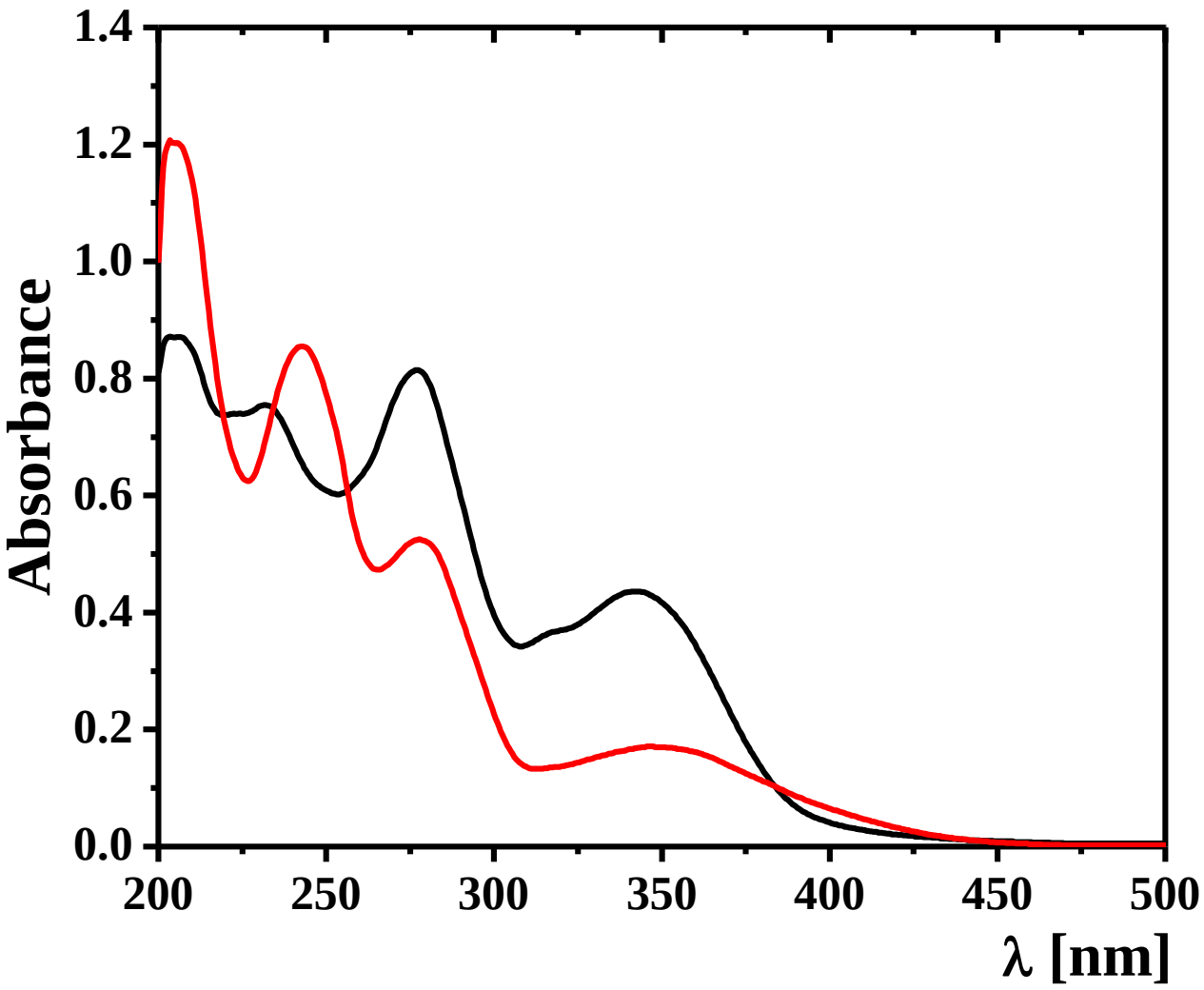


Fig. S4 Absorption spectra of **HBC** (1 μM) and **[Al(HBC)(MeOH)(NO_3)$_3$]** in H_2O:MeOH = 7:3 (v/v).

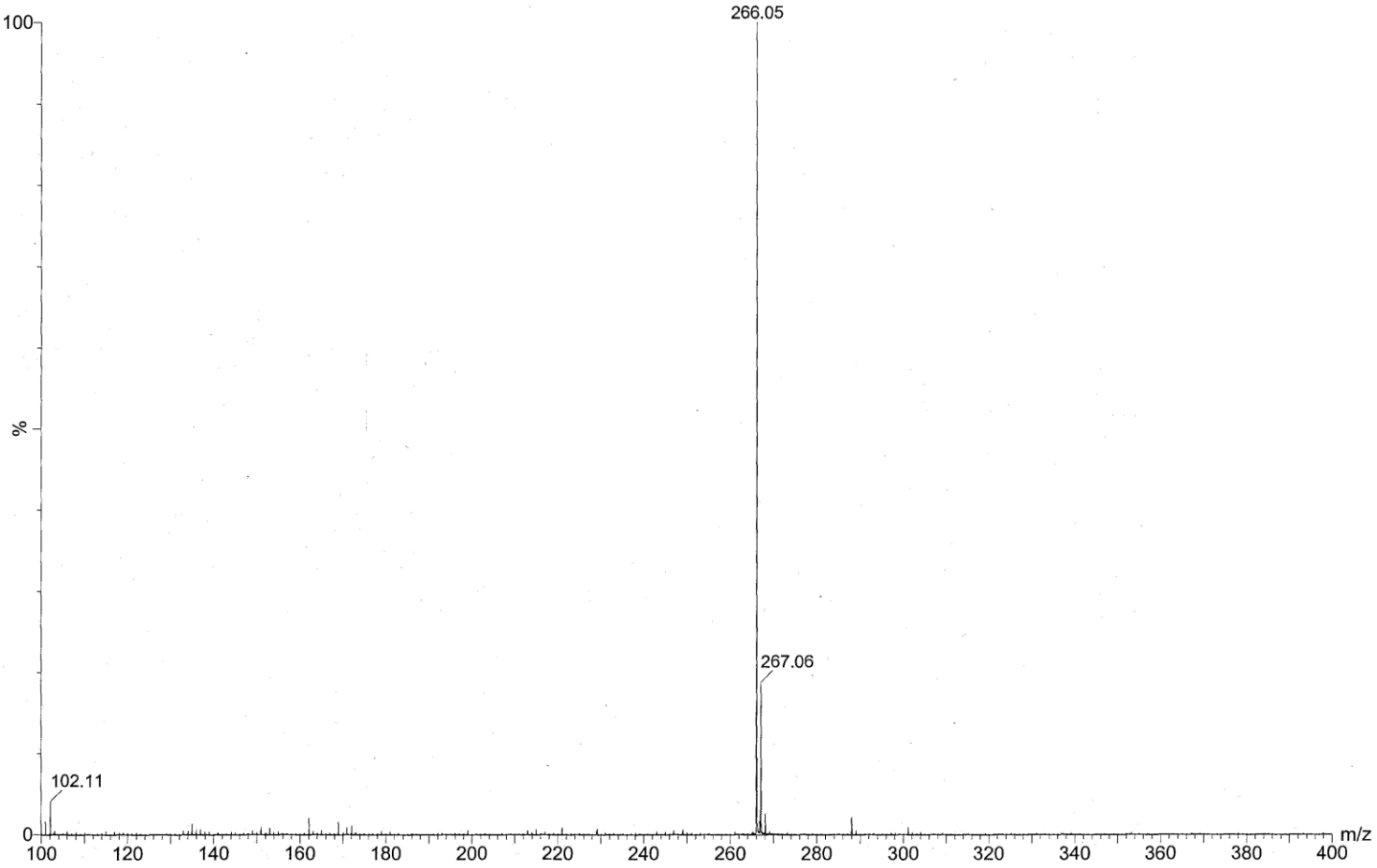


Fig. S5 QTOF-MS ES^+ spectrum of **HBC**.

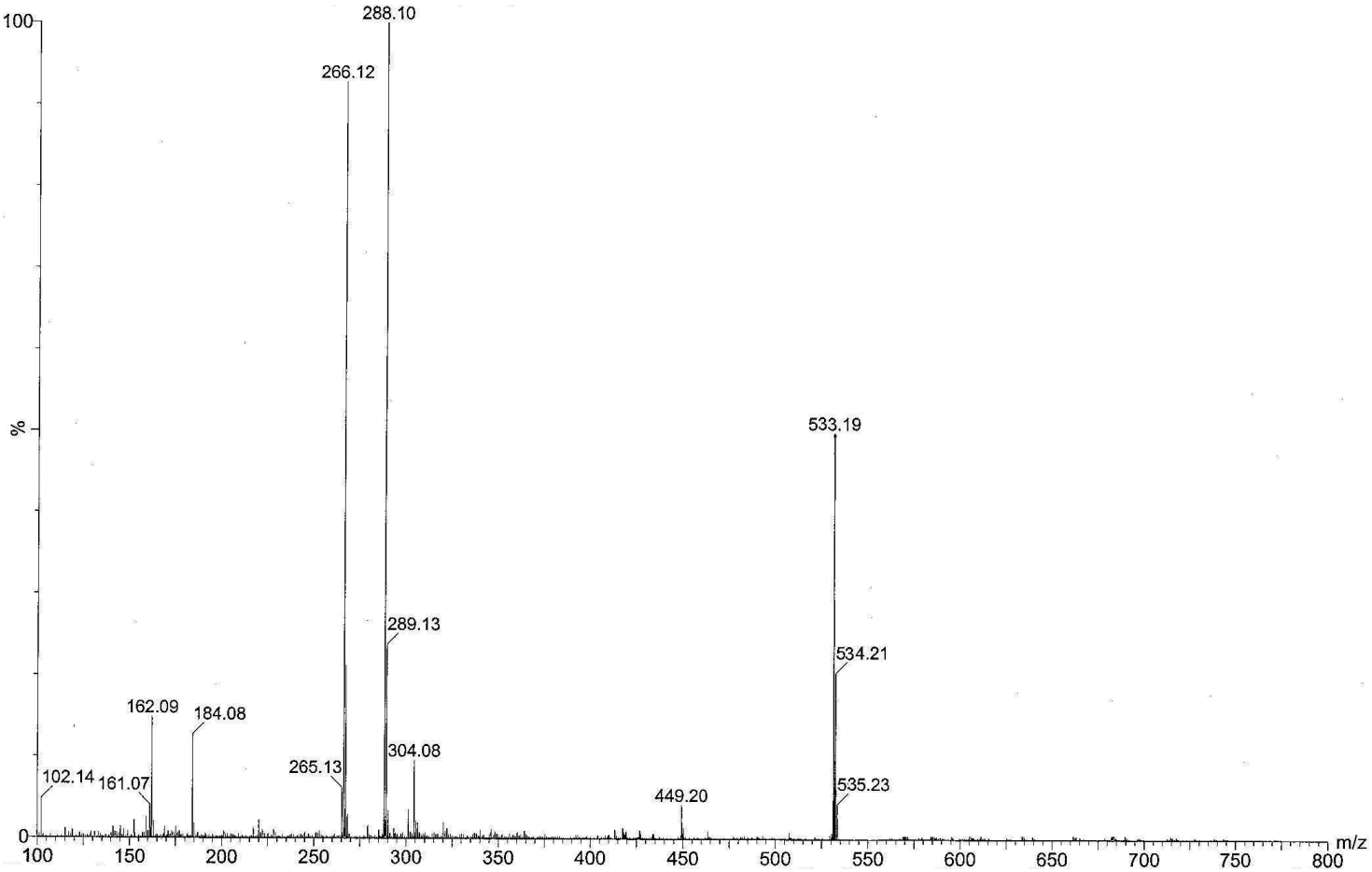
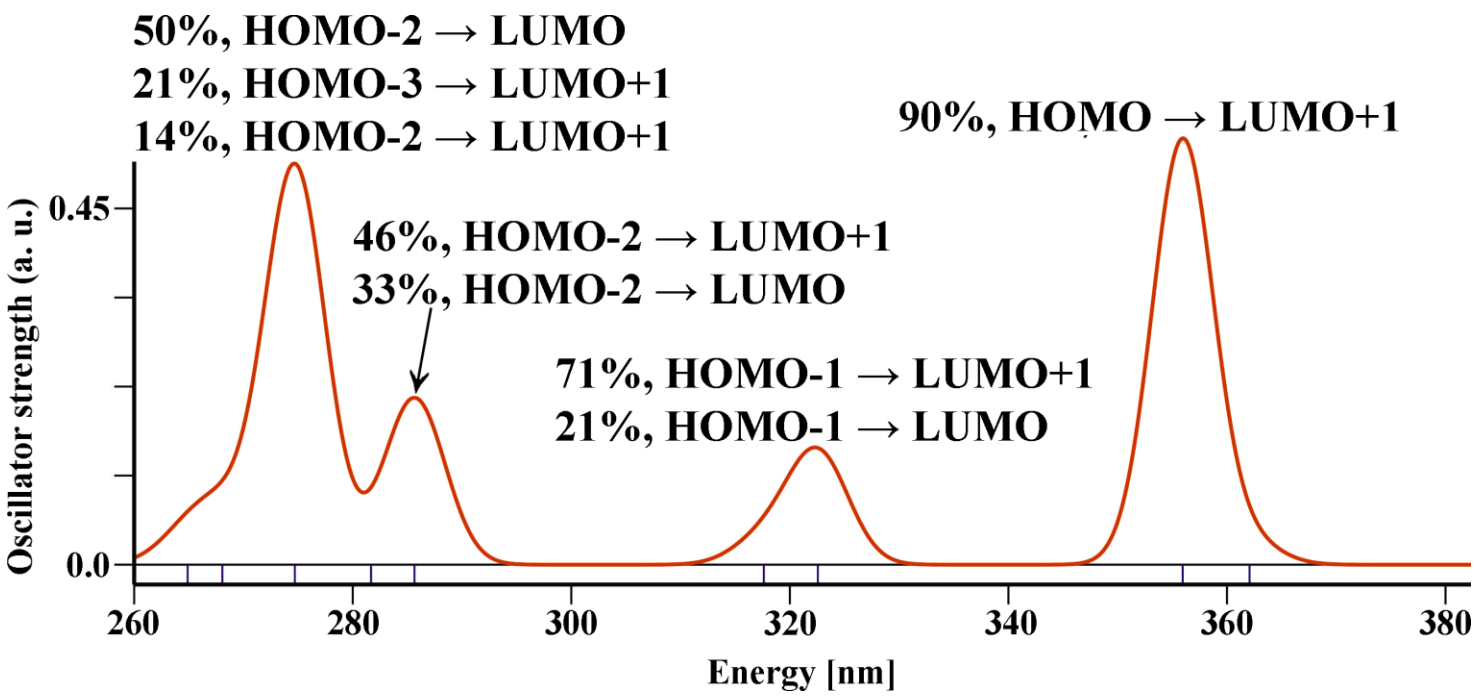
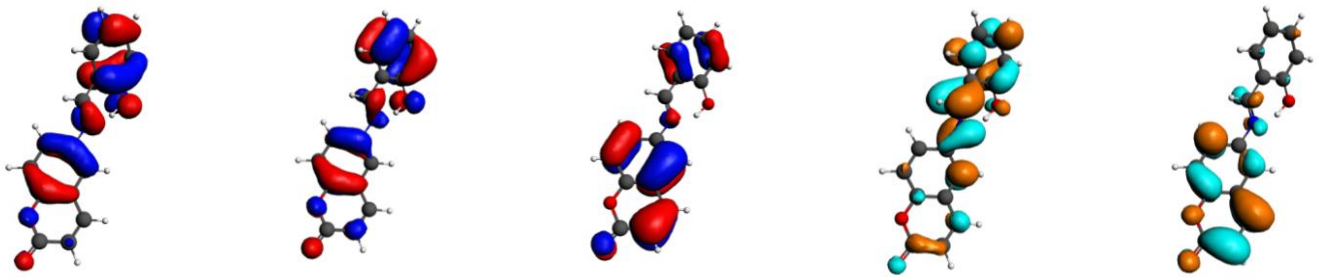


Fig. S6 QTOF-MS ES$^+$ spectrum of **[Al(HBC)(MeOH)(NO$_3$)$_3$]**.

A)



B)



HOMO (–0.2296 a. u.) **HOMO-1 (–0.2464 a.u.)** **HOMO-2 (–0.2659 a. u.)** **LUMO+1 (–0.0851 a. u.)** **LUMO (–0.0877 a. u.)**

Fig. S7 Simulated TD-DFT absorption spectrum (B3LYP/TZP, gas phase) of **HBC** (**A**) together with the contours of molecular orbitals involved in the dominant transitions (**B**).

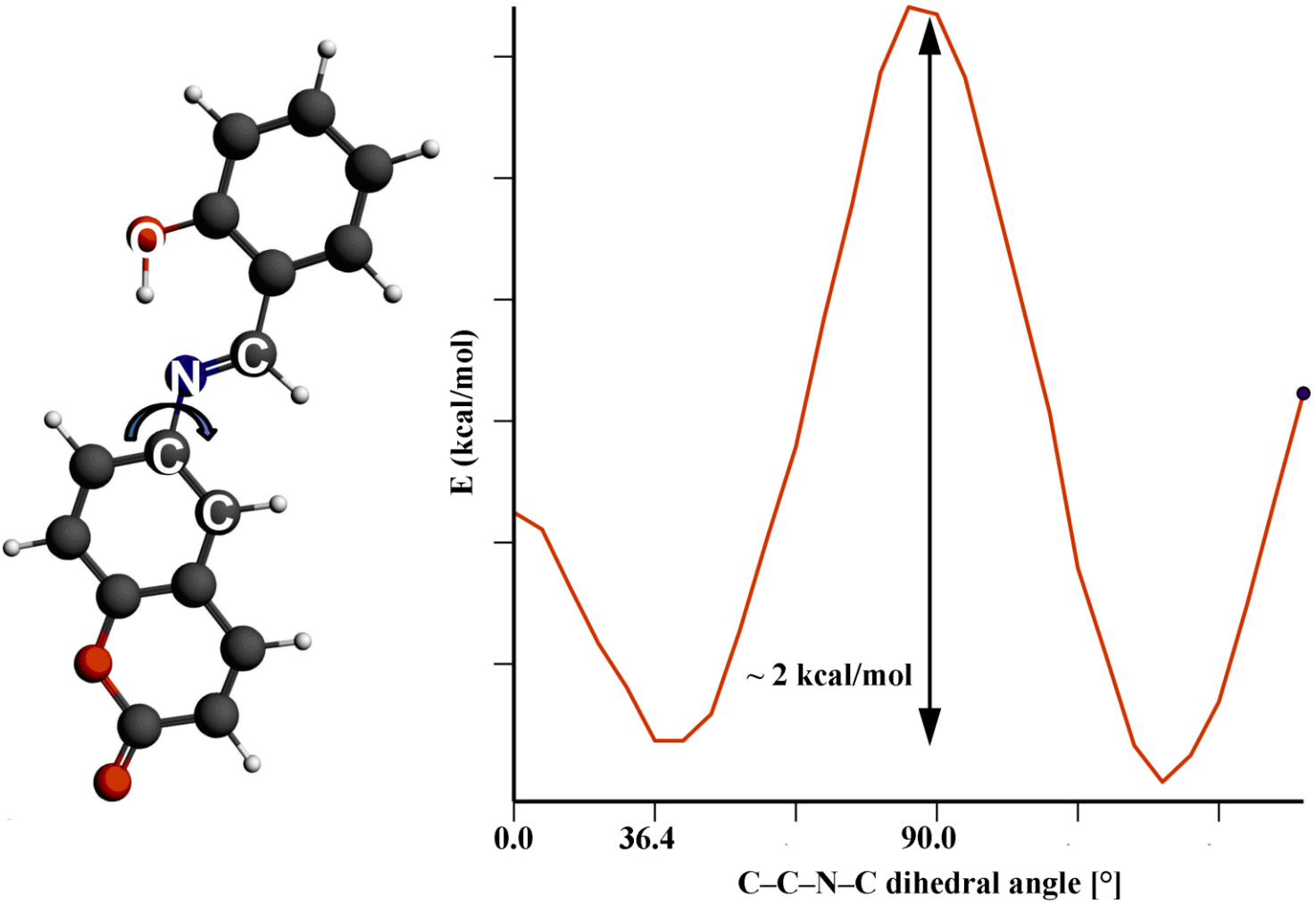


Fig. S8 Energy profile for **HBC**, characterizing rotation around the middle C–N bond (DFT/TZP/BP86). It is clearly shown that the ground state of **HBC** adopts a twisted conformation (∠C–C–N–C = 36.4°) and contains an intramolecular O–H···N hydrogen bond. Twisting is due to the repulsion between the N=C–H and H–C(coumarin).

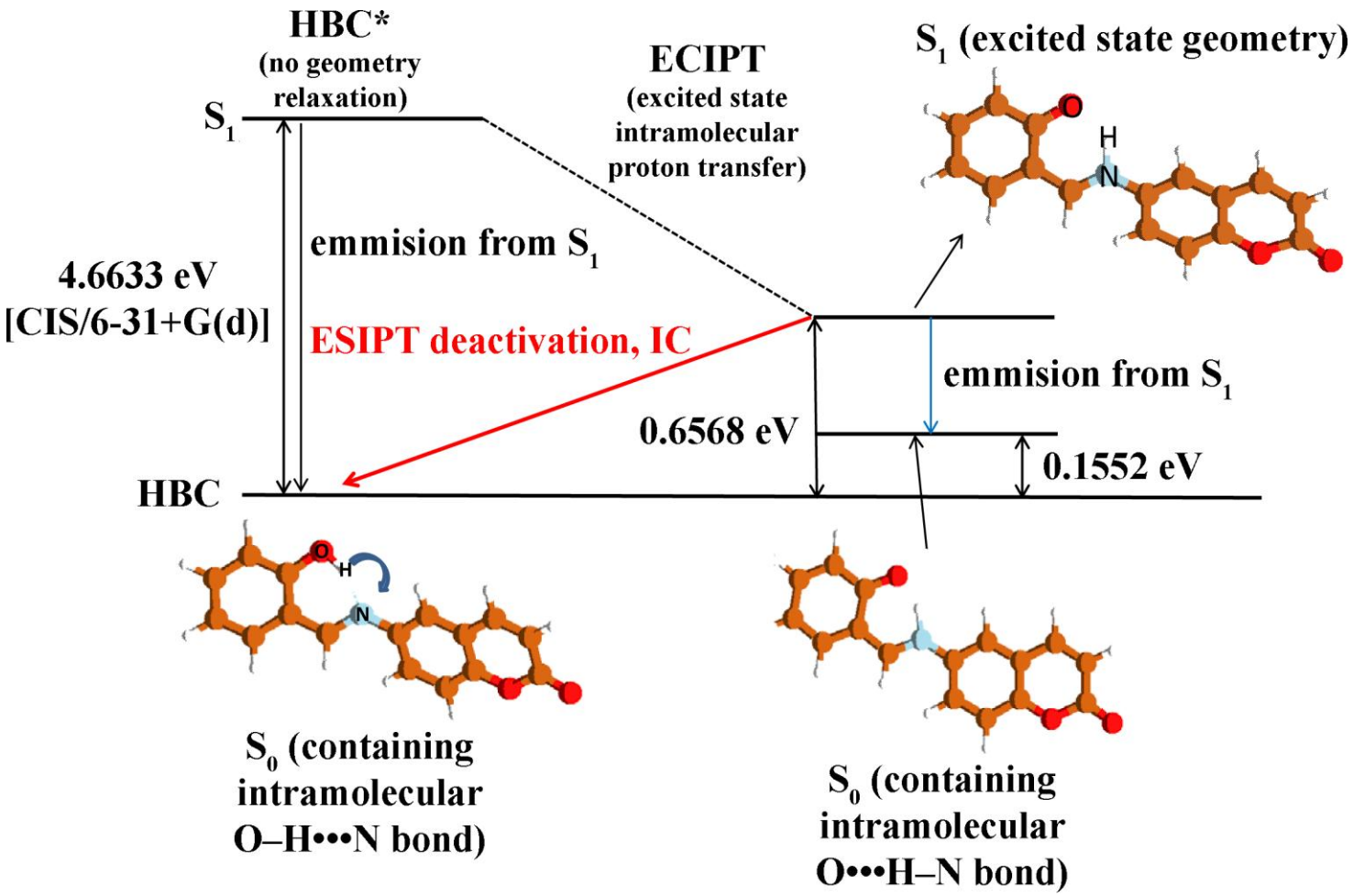
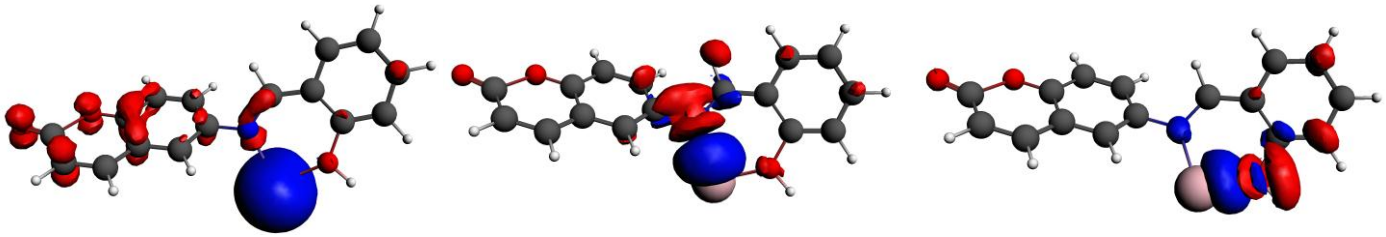


Fig. S9 The four-states model of the absorption/emission processes in **HBC** based on the DFT/BP86/TZP calculation. Possible deactivation of the excited state S_1 *via* internal conversion pathway is highlighted in red color. In addition vertical $S_o \rightarrow S_1$ transition energy based on the CIS [6-31+G(d)] calculations is presented.



–282.9 kcal/mol **–45.2 kcal/mol** **–73.8 kcal/mol**

Fig. S10 Dominating NOCV based deformation density channels, describing the interaction between Al^{3+} and **HBC**.

Table S1 ETS-NOCV based results describing the interaction between cations M^{n+} and **HBC**

M^{n+}/ETS[a]	ΔE_{total}	ΔE_{orb}	ΔE_{elstat}	ΔE_{Pauli}
Al^{3+}	–571.59	–479.90	–124.38	32.68
Zn^{2+}	–248.26	–194.18	–107.99	53.91
Cd^{2+}	–206.13	–165.68	–67.93	24.47
Mg^{2+}	–186.10	–152.46	–87.29	53.66
Ca^{2+}	–135.90	–129.77	–79.16	73.03
Na^{+}	–37.89	–22.25	–32.58	16.95
Pb^{2+}	–147.5	–146.99	–90.54	90.03
Cu^{+}	–84.06	–74.72	–121.84	112.5
K^{+}	–26.68	–18.84	–25.72	17.88
Hg^{2+} [b]	—	—	—	—

[a] $\Delta E_{total} = \Delta E_{orb} + \Delta E_{elstat} + \Delta E_{Pauli}$

[b] no minimum was found for the [**HBC**-Hg^{2+}] complex

Table S2 Selected bond lengths (Å) and bond angles (°) for **HBC**

Molecule A				**Molecule B**			
Bond lengths							
N(1)–C(1)	1.264(4)	C(4)–C(10)	1.421(5)	N(1A)–C(1A)	1.289(4)	C(4A)–C(10A)	1.425(4)
N(1)–C(2)	1.439(4)	C(5)–C(6)	1.379(5)	N(1A)–C(2A)	1.426(4)	C(5A)–C(6A)	1.378(5)
O(1)–C(12)	1.354(4)	C(6)–C(7)	1.381(5)	O(1A)–C(12A)	1.366(4)	C(6A)–C(7A)	1.383(5)
O(2)–C(5)	1.378(4)	C(8)–C(9)	1.454(4)	O(2A)–C(5A)	1.387(4)	C(8A)–C(9A)	1.443(5)
O(2)–C(8)	1.388(4)	C(9)–C(10)	1.356(5)	O(2A)–C(8A)	1.381(4)	C(9A)–C(10A)	1.354(5)
O(3)–C(8)	1.202(4)	C(11)–C(12)	1.406(4)	O(3A)–C(8A)	1.201(4)	C(11A)–C(12A)	1.404(4)
C(1)–C(11)	1.438(5)	C(11)–C(16)	1.410(5)	C(1A)–C(11A)	1.450(5)	C(11A)–C(16A)	1.390(5)
C(2)–C(3)	1.387(5)	C(12)–C(13)	1.397(5)	C(2A)–C(3A)	1.384(5)	C(12A)–C(13A)	1.381(5)
C(2)–C(7)	1.406(4)	C(13)–C(14)	1.369(5)	C(2A)–C(7A)	1.402(4)	C(13A)–C(14A)	1.386(5)
C(3)–C(4)	1.399(5)	C(14)–C(15)	1.404(5)	C(3A)–C(4A)	1.408(5)	C(14A)–C(15A)	1.399(5)
C(4)–C(5)	1.393(4)	C(15)–C(16)	1.382(5)	C(4A)–C(5A)	1.393(4)	C(15A)–C(16A)	1.390(5)
Bond angles							
C(1)–N(1)–C(2)	121.0(3)	O(3)–C(8)–O(2)	116.7(3)	C(1A)–N(1A)–C(2A)	120.9(3)	O(3A)–C(8A)–O(2A)	116.1(3)
C(5)–O(2)–C(8)	121.4(3)	O(3)–C(8)–C(9)	125.7(4)	C(8A)–O(2A)–C(5A)	121.5(3)	O(3A)–C(8A)–C(9A)	126.4(3)
N(1)–C(1)–C(11)	121.6(3)	O(2)–C(8)–C(9)	117.6(3)	N(1A)–C(1A)–C(11A)	122.2(3)	O(2A)–C(8A)–C(9A)	117.4(3)
C(3)–C(2)–C(7)	119.9(3)	C(10)–C(9)–C(8)	120.0(3)	C(3A)–C(2A)–C(7A)	119.9(3)	C(10A)–C(9A)–C(8A)	120.9(3)
C(3)–C(2)–N(1)	116.2(3)	C(9)–C(10)–C(4)	121.5(3)	C(3A)–C(2A)–N(1A)	115.7(3)	C(9A)–C(10A)–C(4A)	121.3(3)
C(7)–C(2)–N(1)	123.9(3)	C(12)–C(11)–C(16)	117.7(3)	C(7A)–C(2A)–N(1A)	124.4(3)	C(16A)–C(11A)–C(12A)	118.7(3)
C(2)–C(3)–C(4)	120.7(3)	C(12)–C(11)–C(1)	121.9(3)	C(2A)–C(3A)–C(4A)	120.5(3)	C(16A)–C(11A)–C(1A)	119.1(3)
C(5)–C(4)–C(3)	118.1(3)	C(16)–C(11)–C(1)	120.4(3)	C(5A)–C(4A)–C(3A)	118.1(3)	C(12A)–C(11A)–C(1A)	122.1(3)
C(5)–C(4)–C(10)	118.0(3)	O(1)–C(12)–C(13)	118.9(3)	C(5A)–C(4A)–C(10A)	117.4(3)	O(1A)–C(12A)–C(13A)	119.2(3)
C(3)–C(4)–C(10)	123.9(3)	O(1)–C(12)–C(11)	121.1(3)	C(3A)–C(4A)–C(10A)	124.5(3)	O(1A)–C(12A)–C(11A)	120.8(3)
O(2)–C(5)–C(6)	116.9(3)	C(13)–C(12)–C(11)	120.0(3)	C(6A)–C(5A)–O(2A)	116.7(3)	C(13A)–C(12A)–C(11A)	120.0(3)
O(2)–C(5)–C(4)	121.3(3)	C(14)–C(13)–C(12)	120.3(4)	C(6A)–C(5A)–C(4A)	121.8(3)	C(12A)–C(13A)–C(14A)	120.5(3)
C(6)–C(5)–C(4)	121.7(3)	C(13)–C(14)–C(15)	121.8(3)	O(2A)–C(5A)–C(4A)	121.4(3)	C(13A)–C(14A)–C(15A)	120.6(3)
C(5)–C(6)–C(7)	120.0(3)	C(16)–C(15)–C(14)	117.3(4)	C(5A)–C(6A)–C(7A)	119.7(3)	C(16A)–C(15A)–C(14A)	118.3(3)
C(6)–C(7)–C(2)	119.6(3)	C(15)–C(16)–C(11)	122.8(4)	C(6A)–C(7A)–C(2A)	120.0(3)	C(11A)–C(16A)–C(15A)	121.9(3)

Table S3 Hydrogen bond lengths (Å) and angles (°) for **HBC**

	D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠(DHA)
Molecule A	O(1)–H(1)···N(1)	0.825(10)	1.87(2)	2.590(4)	145(4)
Molecule B	O(1A)–H(1A)···N(1A)	0.831(10)	1.85(2)	2.616(4)	152(4)

Table S4 ETS energy decomposition based results, describing the interaction between two planar **HBC** units from the crystal structure (BP86-D3/TZ2P method)

ΔE_{total} [a]	ΔE_{orb}	ΔE_{elstat}	ΔE_{Pauli}	$\Delta E_{dispersion}$
–11.42	–3.09	–3.72	10.59	–15.2

[a] $\Delta E_{total} = \Delta E_{orb} + \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{dispersion}$