Supporting Information

A new photochromic Gd-MOF with photoswitchable bluish-white to greenish-yellow emission based on electron transfer

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1. Determination

A PLS-SXE300C 300 W xenon lamp system equipped with an IR filter was used to prepare colored samples, and the distances between these samples and the Xe lamp were around 30 cm.

UV−visible (UV−vis) spectra were recorded at room temperature on a PerkinElmer Lambda 900 UV/vis/NIR spectrophotometer equipped with an integrating sphere in the wavelength range of 200−1200 nm. BaSO4 plates were used as references (100% reflection), on which the finely ground power of each sample was coated. Powder X-ray diffraction (XRD) patterns were collected with a Rigaku MiniFlex II diffractometer powered at 30 kV and 15 mA for Cu Kα (λ = 1.54056 Å). Simulated patterns were produced using the Mercury Version 1.4 software (http://www.ccdc.cam.ac.uk/products/mercury/) and single-crystal reflection diffraction data. Electron spin resonance (ESR) spectra were recorded on a Bruker ER-420 spectrometer with a 100 kHz magnetic field in the X band at room temperature.

X-ray Crystallographic Study. The X-ray diffraction measurement of Gd-MOF was performed on a Rigaku SATURN70 CCD diffractometer using graphite

monochromated Mo Kα radiation (λ = 0.71073 Å). The primitive structures of Gd-MOF was solved by the direct method using the Siemens SHELXTL Version 5 package of crystallographic software.2,3 Difference Fourier maps based on these atomic positions yielded other non-hydrogen atoms. The final structure was refined using a full-matrix least-squares refinement on F2. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms on carbon atoms were generated geometrically. Crystallographic data and structural refinements for the compounds are summarized in Table S1. Important bond distances are listed in Table S2. More details on the crystallographic studies as well as atomic displacement parameters are given as cif Supporting Information.

The entry of CCDC-1974390, 2034511 contains the supplementary crystallographic data for Gd-MOF and Hipbp·**2**H_2O, respectively. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallograp hic Dat a Centre, 12, Uni on Road, Cambridge CB2 1EZ, U.K. Fax: (Internet) +44-1223/336-033. E-mail: deposit@ccdc.cam.ac.uk

2. Synthesis of H_2ipbp and Gd-MOF

The hydrated **H_2ipbpCl** (1-carboxyethyl-4,4'-bipyridine) was synthesized according to the procedure described previously (*Chem. Eur. J.* **2017***, 23,* 18074 – 18083).

The product was dissolved in 7 mL of ethanol and water. After filtration, the filtrate was left for slow evaporation in dark at room temperature. Few Yellow rod-shape crystals **Hipbp·2**H_2O were obtained after one week.

$Gd(NO_3)_3{\cdot}(H_2O)_6$ (45 mg, 0.1 mmol) and H_2ipbpCl (30 mg, 0.05 mmol) were dissolved in a mixture of DMF (1 mL) and H_2O (0.5 mL). The solution was sealed in a 20 mL vial and heated at 100°C for 48 hours, then cooled to room temperature. Light yellow shuttle-shaped crystals of **Gd-MOF** were collected by filtration with a 40 wt% yield based on H_2ipbpCl.

3. Graphics

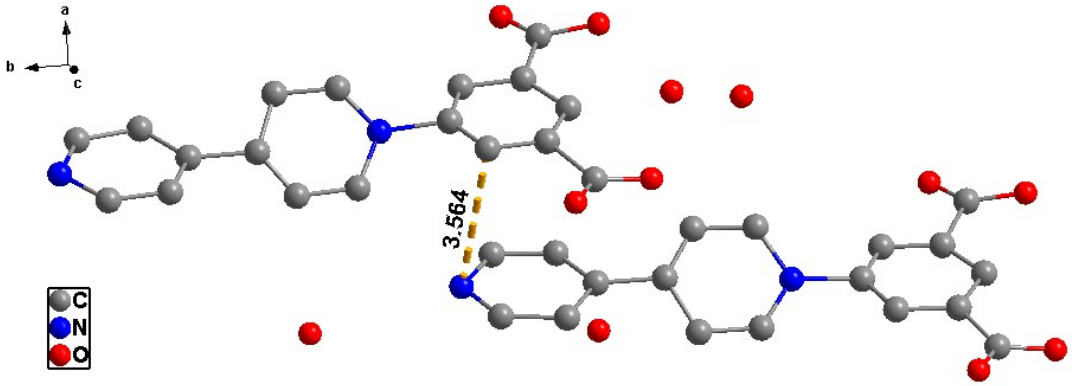

Figure S1. The molecular structure of the ligand Hipbp·**2**H_2O.

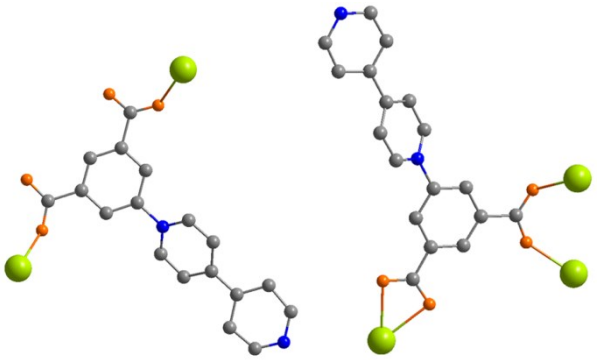

Figure S2. The different kinds of bridging modes of ipbp$^-$ ligand.

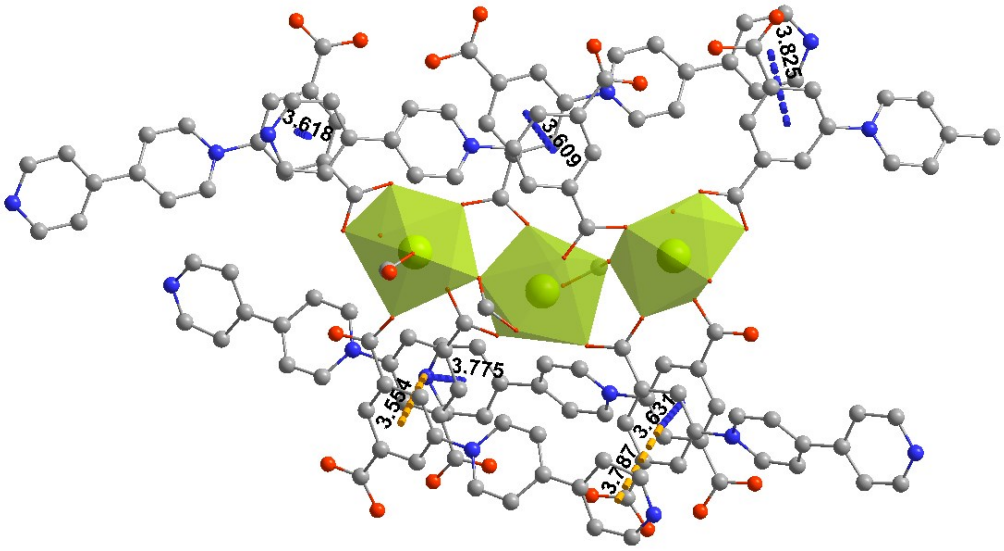

Figure S3. The $\{Gd_3(COO)_3(OH)_2\}^{4+}$ core connected with the eight ipbp ligands and π–π stacking of ipbp ligands between adjacent molecules with centroid-to-centroid distances of 3.554–3.787 Å.

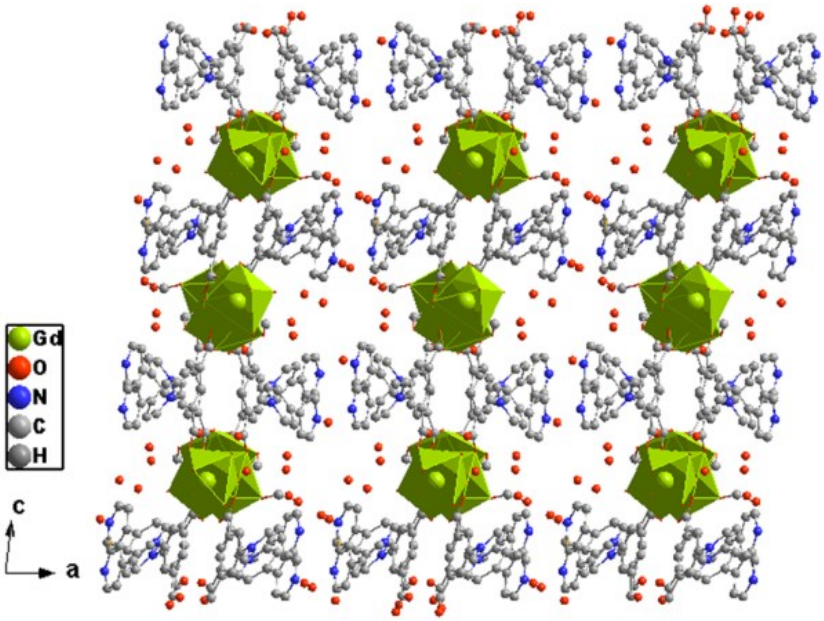

Figure S4. The stacking 2D layers of **Gd-MOF** along the a-axis. (color scheme: Gd green, O red, N blue, C gray).

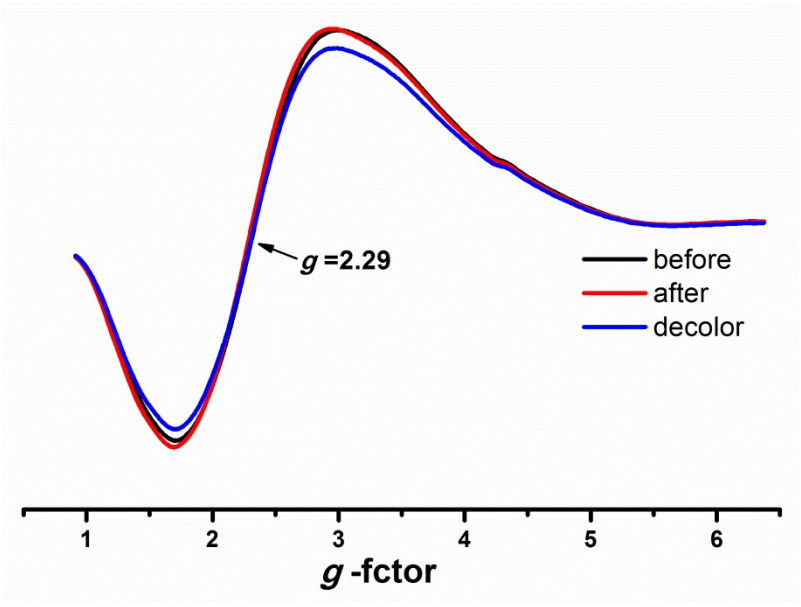

Figure S5. EPR signals of the original and UV irradiated samples for compound Gd.

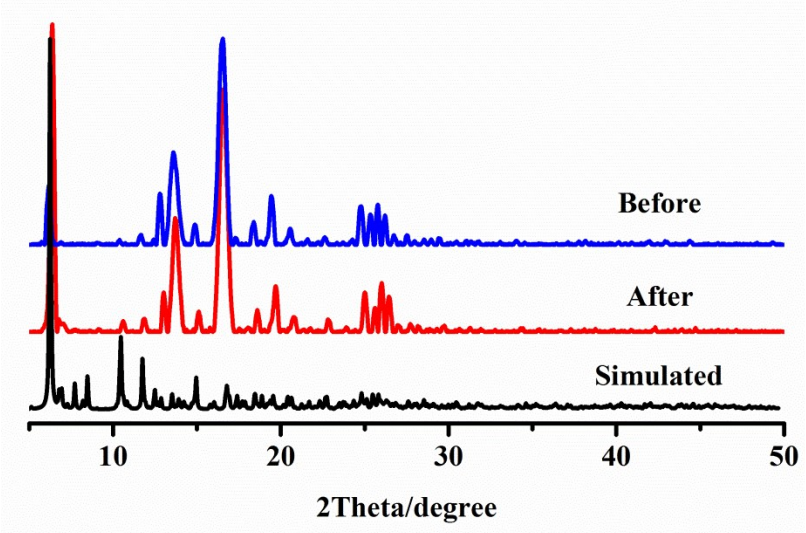

Figure S6. PXRD patterns of **Gd-MOF**.

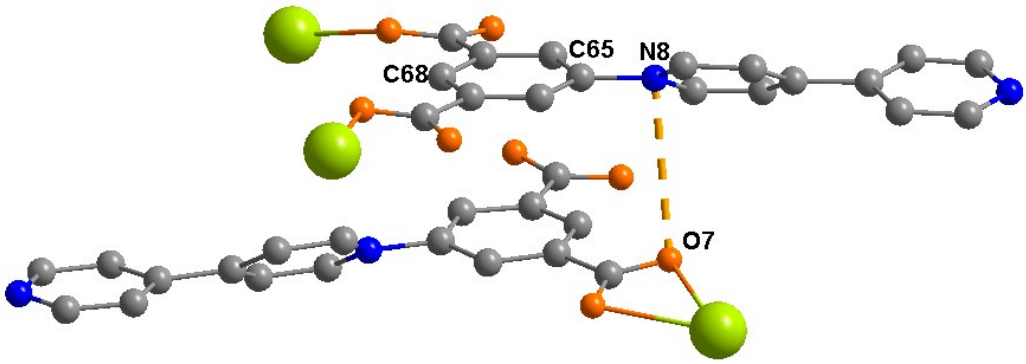

Figure S7. The shortest one of O7–N8 is 3.62 Å and the dihedral angle between O7–N8–C65 is 94.01.

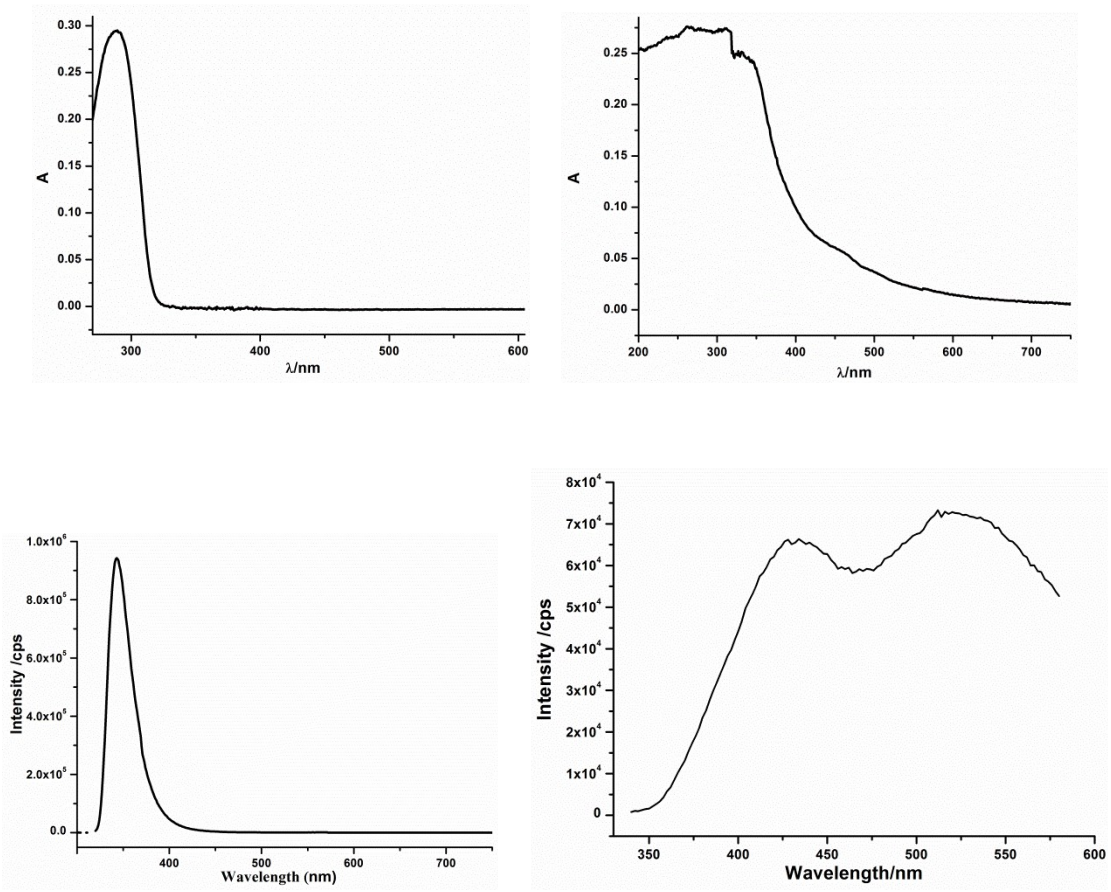

Figure S8. UV-vis absorption spectra of Hipbp ligand in the liquid and solid. PL emission spectra of Hipbp in the liquid or solid state at room temperature.

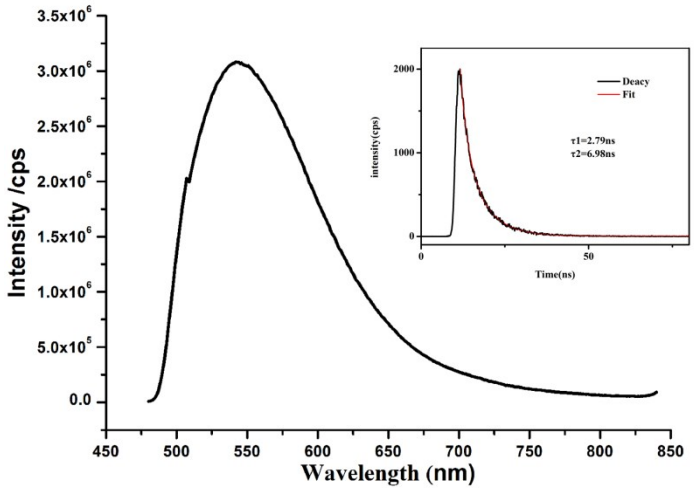

Figure S9. PL emission spectra of Hipbp (ex = 460 nm) in solid state at room temperature and the life time.

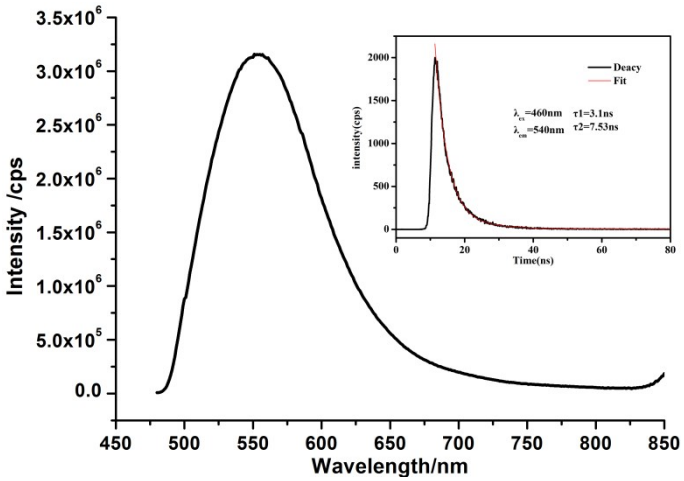

Figure S10. PL spectra of **Gd-MOF** (ex = 460 nm) in the solid state at room temperature and the life time**.**

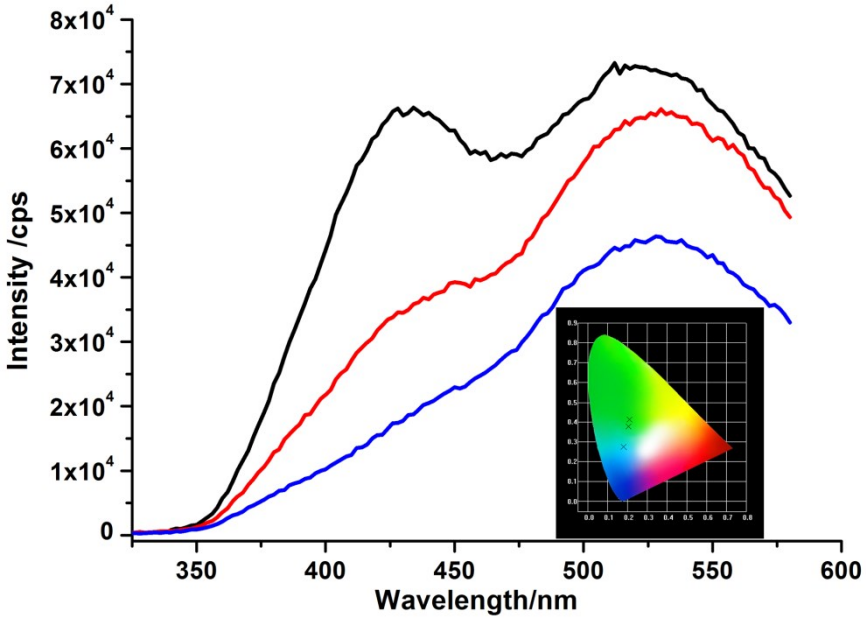

Figure S11. In situ time-dependent PL spectra of Hipbp (ex = 300 nm) in the solid state at room temperature, CIE = (0.18, 0.28), (0.21, 0.38) and (0.21, 0.41), respectively.

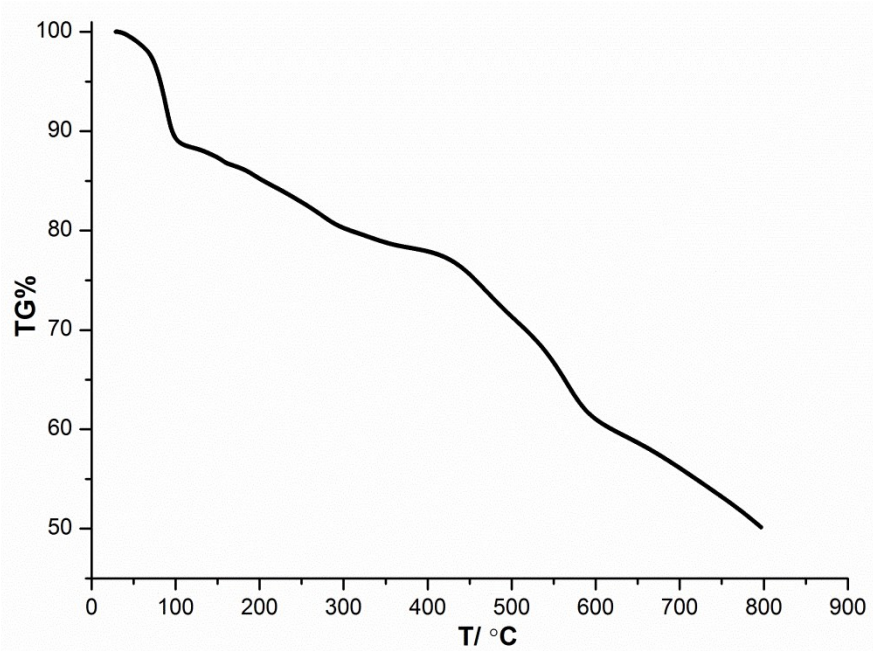

Figure S12. TG curves of **Gd-MOF**.

Table 1. Crystal data and structural refinements for **Gd-MOF** and Hipbp ligand.

Formula	**Hipbpy·2H$_2$O**	**[Gd$_3$(ipbp)$_4$(OH)$_2$(COO)$_3$(H$_2$O)$_2$]·xH$_2$O**
Fw	356.33	802.07
Crystal system	monoclinic	triclinic
Space group	P2$_1$/n	$P\bar{1}$ (No.2)
a **/Å**	8.0723(4)	14.3007(7)
b **/Å**	17.6758(7)	17.1091(5)
c **/Å**	11.6674(6)	18.9641(7)
α **/°**	90	88.689(3)
β **/°**	93.046(5)	83.151(3)
γ **/°□**	90	70.462(4)
V **/Å^3**	1662.40(14)	4340.9(3)

Z	4	2
D_c **/g.cm^{-3}**	1.424	1.627
μ **/mm^{-1}**	0.109	2.357
Goodness-of-fit on F^2	1.255	1.033
R_1, wR_2 **[$I > 2\sigma(I)$]**	0.0555, 0.1594	0.0632, 0.1589
R_1, wR_2 **(all data)**	0.0698, 0.1669	0.0933, 0.1796

$R_1 = \sum||F_o|-|F_c||/\sum|F_o|$, $wR_2 = \{\sum w[(F_o)^2-(F_c)^2]^2/\sum w[(\underline{F}_o)^2]^2\}^{1/2}$.

Table S2. Important bond lengths (Å) for **Gd-MOF and** Hipbp·2H_2O.

$[Gd_3(ipbp)_4(OH)_2(COO)_3(H_2O)_2]\cdot xH_2O$ (1)			
Gd(1)–O(19)	2.413(6)	Gd(2)–O(19) #2	2.480(6)
Gd(1)–O(14)	2.334(6)	Gd(2)–O(13) #2	2.342(6)
Gd(1)–O(16) #1	2.522(6)	Gd(2)–O(22)	2.508(7)
Gd(1)–O(1)	2.307(7)	Gd(2)–O(11) #3	2.321(6)
Gd(1)–O(15) #1	2.449(6)	Gd(2)–O(5)	2.308(6)
Gd(1)–O(18)	2.363(8)	Gd(2)–O(3)	2.342(7)
Gd(1)–O(4) #2	2.411(7)	Gd(2)–O(20) #2	2.486(8)
Gd(1)–O(4W)	2.393(7)	Gd(2)–O(21)	2.391(8)
Gd(3)–O(12) #3	2.372(7)	Gd(3)–O(84)	2.555(7)
Gd(3)–O(22)	2.446(7)	Gd(3)–O(6)	2.312(7)
Gd(3)–O(9)	2.291(7)	Gd(3)–O(3W)	2.402(9)
Gd(3)–O(74)	2.443(7)	Gd(3)–O(2W)	2.351(9)
N(2)–C(7)	1.321(12)	N(6)–C(47)	1.446(12)
N(2)–C(11)	1.455(12)	N(6)–C(46)	1.340(12)
N(2)–C(9)	1.355(12)	N(6)–C(44)	1.364(13)
N(4)–C(29)	1.451(11)	N(8)–C(65)	1.466(11)
N(4)–C(26)	1.328(12)	N(8)–C(63)	1.329(13)
N(4)–C(28)	1.359(12)	N(8)–C(62)	1.350(13)
N(1)–C(1)	1.26(2)	N(3)–C(21)	1.297(17)

N(1)–C(3)	1.30(2)	N(3)–C(19)	1.348(19)
N(5)–C(41)	1.281(17)	N(7)–C(59)	1.373(16)
N(5)–C(37)	1.342(18)	N(7)–C(55)	1.337(15)
C(68)–C(67)	1.393(12)	C(25)–C(24)	1.394(14)
C(68)–C(69)	1.388(12)	C(25)–C(26)	1.381(13)
C(15)–C(18)	1.465(13)	C(65)–C(70)	1.393(13)
C(15)–C(14)	1.399(12)	C(10)–C(9)	1.370(14)
C(15)–C(16)	1.406(13)	C(10)–C(6)	1.387(15)
C(31)–C(30)	1.414(12)	C(8)–C(6)	1.398(14)
C(31)–C(35)	1.493(12)	C(59)–C(58)	1.343(15)
C(31)–C(32)	1.377(12)	C(66)–C(65)	1.378(13)
C(56)–C(55)	1.365(15)	C(48)–C(47)	1.371(13)
C(5)–C(4)	1.405(17)	C(29)–C(34)	1.389(13)
C(5)–C(2)	1.410(17)	C(52)–C(47)	1.377(13)
C(20)–C(19)	1.335(17)	C(42)–C(39)	1.484(14)
C(41)–C(40)	1.394(16)	C(42)–C(45)	1.376(15)
C(38)–C(37)	1.430(17)	C(42)–C(43)	1.363(15)
C(4)–C(3)	1.43(2)	C(33)–C(32)	1.381(13)
C(2)–C(1)	1.387(19)	C(33)–C(34)	1.384(13)
C(60)–C(57)	1.499(13)	C(36)–C(33)	1.491(13)
C(60)–C(61)	1.359(14)	C(50)–C(49)	1.381(13)
C(57)–C(56)	1.393(15)	C(72)–C(69)	1.497(12)
C(28)–C(27)	1.350(14)	C(69)–C(70)	1.386(12)
C(44)–C(43)	1.360(15)	C(53)–C(49)	1.509(12)
C(62)–C(61)	1.375(14)	C(7)–C(8)	1.372(14)
C(22)–C(21)	1.401(16)	C(16)–C(11)	1.368(12)
C(6)–C(5)	1.439(15)	C(12)–C(11)	1.395(12)
C(24)–C(23)	1.497(13)	C(49)–C(48)	1.403(13)
C(24)–C(27)	1.395(14)	C(13)–C(14)	1.367(12)

C(23)–C(22)	1.388(15)	C(13)–C(12)	1.380(13)
C(23)–C(20)	1.365(15)	C(13)–C(17)	1.529(12)
C(58)–C(57)	1.384(14)	C(67)–C(71)	1.491(11)
C(63)–C(64)	1.368(14)	C(67)–C(66)	1.377(12)
C(39)–C(40)	1.387(16)	C(51)–C(50)	1.382(12)
C(39)–C(38)	1.363(16)	C(51)–C(52)	1.375(13)
C(45)–C(46)	1.359(15)	C(51)–C(54)	1.510(13)
C(64)–C(60)	1.384(15)	C(30)–C(29)	1.370(12)
O(19)–C(74)	1.264(13)	O(4)–C(18)	1.264(11)
O(13)–C(72)	1.238(10)	O(3)–C(18)	1.259(12)
O(14)–C(72)	1.257(11)	O(20)–C(74)	1.253(13)
O(16)–C(71)	1.253(11)	O(9)–C(54)	1.236(12)
O(12)–C(53)	1.246(11)	O(7)–C(36)	1.247(12)
O(1)–C(17)	1.231(12)	O(8)–C(36)	1.245(11)
O(22)–C(75)	1.275(15)	O(6)–C(35)	1.282(11)
O(15)–C(71)	1.254(11)	C(54)–O(10)	1.245(14)
O(18)–C(73)	1.214(15)	O(17)–C(73)	1.239(16)
O(11)–C(53)	1.255(11)	O(21)–C(75)	1.358(15)
O(5)–C(35)	1.243(10)	C(17)–O(2)	1.199(13)

Symmetry transformations used to generate equivalent atoms: #1 1-x, 1-y, 2-z; #2 1-x, 1-y, 1-z; #3 1-x, 2-y, 1-z; #4 1-x, 2-y ,-z

Hipbp·2H$_2$O			
O(4)–C(17)	1.2365(14)	C(18)–C(16)	1.3934(14)
O(2)–C(13)	1.3018(13)	C(16)–C(17)	1.5203(14)
O(3)–C(17)	1.2704(14)	N(1)–C(10)	1.327(2)
O(1)–C(13)	1.2154(14)	N(1)–C(1)	1.332(2)
N(2)–C(11)	1.4498(13)	C(7)–C(8)	1.3709(15)

N(2)–C(7)	1.3494(14)	C(6)–C(5)	1.3720(15)
N(2)–C(6)	1.3515(14)	C(4)–C(5)	1.3966(17)
C(11)–C(12)	1.3882(14)	C(4)–C(3)	1.4799(15)
C(11)–C(18)	1.3894(14)	C(4)–C(8)	1.3946(17)
C(12)–C(14)	1.3945(14)	C(3)–C(9)	1.3923(18)
C(13)–C(14)	1.5048(14)	C(3)–C(2)	1.3888(19)
C(14)–C(15)	1.3965(14)	C(9)–C(10)	1.3855(17)
C(15)–C(16)	1.3930(14)	C(2)–C(1)	1.3924(18)