Supporting information for *Dalton Trans.*

First example of Tb_3-containing metallopolymer-type hybrid materials with efficient and high color-purity green luminescence

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Supporting information

Synthesis of PMMA in activation with AIBN

The homogeneous polymerization of MMA in activation with AIBN for comparison was carried out in a Fisher–Porter glass reactor and protected by nitrogen according to the standard radical polymerization procedure. To a solution of MMA (2 mL, 19 mmol) in dry 1,2-dichlorobenzene (15 mL), AIBN initiator (46.0 mg, 1.5 mol% of the monomer) was added, and the resultant homogeneous solution was purged with N_2 for 10 min and sealed under a reduced N_2 atmosphere. The mixture was heated to 80 ^oC with continuous stirring for 24 h. The viscous mixture was diluted with dry 1,2-dichlorobenzene (10 mL) and precipitated with absolute diethyl ether (100 mL) for three times. The resulting solid product of PMMA was collected by filtration and dried at 45 ^oC under vacuum to constant weight. Yield: 91%. IR (KBr, cm^{-1}): 3000 (w), 2951 (m), 2843 (w) 1728 (s), 1631 (m), 1602 (m), 1485 (w), 1454 (w), 1433 (w), 1398 (m), 1384 (m), 1337 (w), 1269 (w), 1238 (w), 1138 (vs), 993 (m), 914 (w), 840 (m), 808 (w), 750 (m), 617 (w), 544 (w), 513 (w), 482 (w). ^1H NMR (400 MHz, DMSO-δ_6-$CDCl_3$ (v/v = 10:1)): δ (ppm) 3.57 (s, 3H, -COOMe), 1.85 (b, 2H, -CH_2-), 0.91 (m, 3H, -CH_3).

Synthesis of PNBE in activatation with H-Grubbs II

The homogeneous polymerization in activation with H-Grubbs II for comparison was carried out in a Fisher–Porter glass reactor and protected by nitrogen according to the typical ROMP procedure. To a solution of NBE (70 mg, 0.75 mmol) in absolute $CHCl_3$ (15 mL), H-Grubbs II initiator (1.1 mg, 1.5 mol-% of NBE) was added in three times (0.6 mg, 0.3 mg and 0.2 mg),

and the resultant mixture was purged with N_2 for 10 min and sealed under a reduced N_2 atmosphere. After the homogeneous solution was continuously stirred at room temperature for 24 h, ethyl vinyl ether (100 μL) was added to quench the reaction. The viscous mixture was diluted with absolute THF (20 mL) and dried at 45 ^{o}C under vacuum to constant weight. For **PNBE**: Yield: 92%. IR (KBr, cm^{-1}): 2924 (m), 2853 (s), 1944 (w), 1450 (s), 1432 (s), 1401 (w), 1370 (w), 1346 (w), 1303 (w), 1180 (w), 1069 (w), 1028 (w), 996 (w), 941 (w), 735 (s), 698 (vs), 540 (w). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.33 (s, =CH-), 2.42 (s, -CH), 1.81 (m, $-CH_2$), 1.29 (m, $-CH_2$), 1.03 (m, $-CH_2$).

Captions to Tables 1-2S and Figures 1-3S

Table 1S Selected bond lengths (Å) and bond angles (°) for **3**·2MeOH·4H_2O

Table 2S GPC data of the samples of **PMMA**, **PNBE** and the series of metallopolymers **Poly(NBE-1)**, **Poly(NBE-2)**, **Poly(NBE-3)** and **Poly(NBE-4)**

Figure 1S Perspective drawing of the weak N1-H1···Cl5 H-bonding (3.045(2) Å) interaction between the host framework and the free Cl5 in complex **3**·2MeOH·4H_2O.

Figure 2S Visible emission and excitation spectra of complex **4** in MeCN solution at 1×10^{-5} M and the hybrid materials **4@PMMA** and **Poly(NBE-4)** with the feeding molar ratio of 400:1 in solid state at 77 K.

Table 1S

3·2MeOH·4H_2O			
Tb(1)-O(1)	2.396(12)	Tb(2)-O(7)	2.326(11)
Tb(1)-O(2)	2.525(14)	Tb(2)-O(8)	2.588(13)
Tb(1)-O(5)	2.313(13)	Tb(2)-N(2)	2.454(15)
Tb(1)-O(10)	2.395(15)	Tb(2)-N(4)	2.473(14)
Tb(1)-N(6)	2.518(15)	Tb(3)-O(3)	2.349(10)
Tb(1)-Cl(1)	2.648(6)	Tb(3)-O(4)	2.472(13)
Tb(1)-Cl(2)	2.706(7)	Tb(3)-O(7)	2.290(12)
Tb(2)-O(1)	2.344(12)	Tb(3)-O(9)	2.406(12)
Tb(2)-O(3)	2.333(11)	Tb(3)-N(8)	2.492(16)
Tb(2)-O(5)	2.325(11)	Tb(3)-Cl(3)	2.692(5)
Tb(2)-O(6)	2.575(13)	Tb(3)-Cl(4)	2.689(5)
Tb(1)-Tb(2)	3.856(3)	Tb(2)-Tb(3)	3.837(4)
C(9)-C(10)	1.304(19)	C(43)-C(44)	1.297(10)
C(26)-C(27)	1.302(10)	C(60)-C(61)	1.303(10)
N(1)-H(1)···Cl(5)	3.045(2)		
O(1)-Tb(1)-O(2)	63.8(4)	O(3)-Tb(3)-O(4)	66.2(4)
O(1)-Tb(1)-O(5)	68.8(4)	O(3)-Tb(3)-O(7)	68.5(4)
O(5)-Tb(1)-N(6)	71.5(4)	O(7)-Tb(3)-N(8)	73.5(5)
O(5)-Tb(2)-O(6)	63.9(4)	O(1)-Tb(2)-N(2)	73.0(5)
O(7)-Tb(2)-O(8)	63.4(4)	O(3)-Tb(2)-N(4)	72.2(4)

Table 2S

Sample	Monomer	NBE/Complex	M_n[a]/g·mol	PDI[b]
PMMA	MMA	-	45255	1.15
PNBE	NBE	-	24302	2.03
Poly(NBE-1)	NBE/**1**	400:1	20020	2.23
Poly(NBE-2)	NBE/**2**	400:1	21073	2.11
Poly(NBE-3)	NBE/**3**	200:1	23625	2.17
Poly(NBE-3)	NBE/**3**	400:1	24125	2.21
Poly(NBE-3)	NBE/**3**	600:1	25778	2.26
Poly(NBE-3)	NBE/**3**	800:1	25592	2.32
Poly(NBE-4)	NBE/**4**	400:1	22912	2.58

[a] M_n is the number average molecular weight.

[b] PDI = M_w/M_n, where M_w is the weight average molecular weight.

Figure 1S

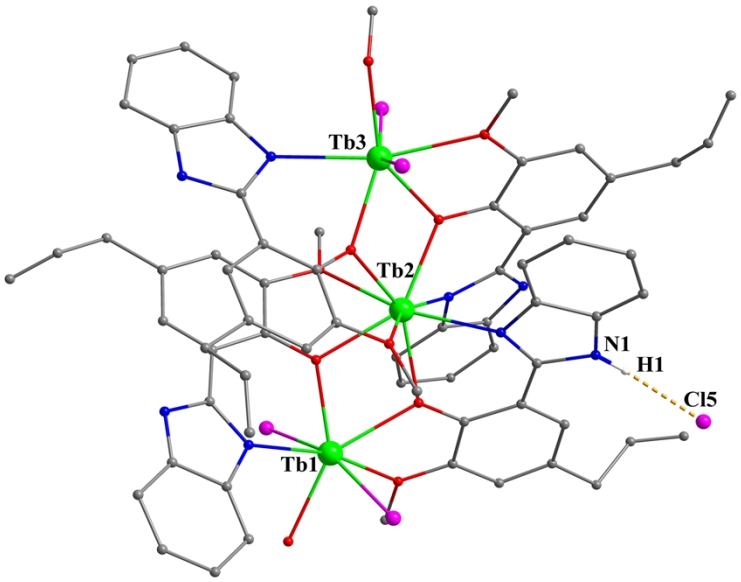

Figure 2S