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四卤化锰(II)配合物的结构调控及力致发光性能

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Structural Manipulation and Triboluminescence of Tetrahalomanganese(II) Complexes

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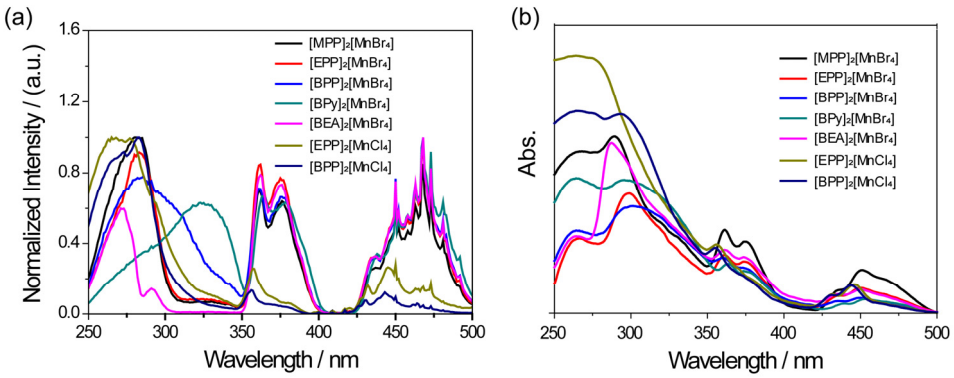

图 S1　298 K 下固态锰配合物的激发光谱(归一化) (a)和紫外-可见吸收光谱(b)

Fig. S1　The normalized excitation spectra (a) and UV-Vis absorption spectra (b) of solid state manganese(II) complexes measured at 298 K.

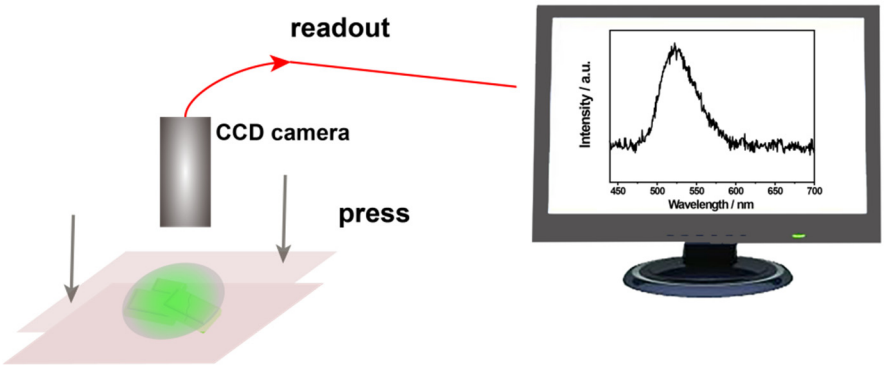

图 S2　TL 测试实验设备(CCD 探测器：积分时间 = 1000 ms，平均次数 = 2 次)

Fig. S2　Experimental setups for TL measurements (CCD camera: exposure time = 1000 ms, averaging = 2 times).

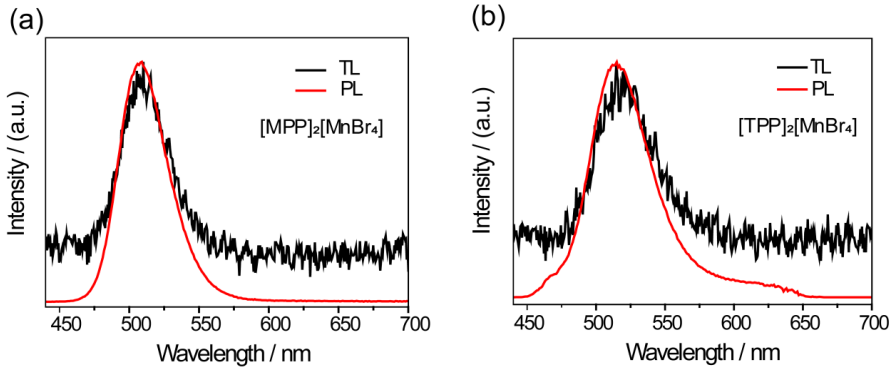

图 S3　锰(II)配合物[MPP]$_2$[MnBr$_4$] (a)和[TPP]$_2$[MnBr$_4$] (b)的 TL 和 PL 光谱(归一化)

Fig. S3　The normalized TL and PL spectra of manganese(II) complexes [MPP]$_2$[MnBr$_4$] (a) and [TPP]$_2$[MnBr$_4$] (b).

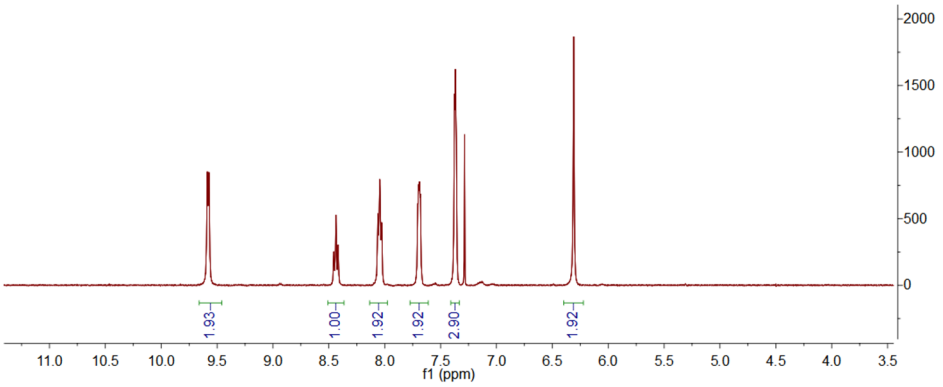

图 S4　配体 BPyBr 的核磁共振氢谱图

Fig. S4　The ^{1}H NMR spectrum of ligand BPyBr.

表 S1　配合物[BEA]$_2$[MnBr$_4$]、[EPP]$_2$[MnCl$_4$]、[BPP]$_2$[MnCl$_4$]、[BPP]$_2$[MnBr$_4$]和[BPy]$_2$[MnBr$_4$]的晶体学数据

Table S1　The crystallographic data for complexes [BEA]$_2$[MnBr$_4$], [EPP]$_2$[MnCl$_4$], [BPP]$_2$[MnCl$_4$], [BPP]$_2$[MnBr$_4$] and [BPy]$_2$[MnBr$_4$].

Complex	[BEA]$_2$[MnBr$_4$]	[EPP]$_2$[MnCl$_4$]	[BPP]$_2$[MnCl$_4$]	[BPP]$_2$[MnBr$_4$]	[BPy]$_2$[MnBr$_4$]
CCDC	1937750	1889594	1937752	1937749	1937751
Empirical Formula	$C_{26}H_{44}Br_4MnN_2$	$C_{40}H_{40}Cl_4MnP_2$	$C_{50}H_{44}Cl_4MnP_2$	$C_{50}H_{44}Br_4MnP_2$	$C_{24}H_{24}Br_4MnN_2$
Formula Weight	759.21	779.40	903.53	1081.37	715.03
Crystal System	monoclinic	monoclinic	orthorhombic	triclinic	monoclinic
Space Group	$P2_1/c$	Cc	$Pbca$	P-1	$C2/c$
a (Å)	17.347(2)	12.223(3)	20.764(5)	10.726(9)	25.083(4)
b (Å)	10.5867(16)	20.914(4)	18.434(5)	12.720(11)	25.285(4)
c (Å)	18.235(3)	16.393(3)	23.251(6)	18.689(15)	16.957(4)
α (°)	90	90	90	106.16(2)	90
β (°)	113.408(4)	110.772(5)	90	92.91(2)	96.161(5)
γ (°)	90	90	90	93.45(2)	90
V (Å^3)	3073.3(8)	3918.1(14)	8900(4)	2439(4)	10692(3)
Z value	4	32	8	2	16
D(calcd) (g cm^{-3})	1.641	2.039	1.349	1.473	1.777
Temperature (K)	297.68	297.19	296.05	295.58	295.15
μ (mm^{-1})	5.647	3.392	0.643	3.645	6.487
F(000)	1516.0	2304.0	3736.0	1078.0	5552.0
R_1, wR_2 [$I > 2\sigma(I)$]	0.0380, 0.0681	0.0423, 0.0951	0.0461, 0.0957	0.1222, 0.2683	0.0953, 0.1493

1 Å = 0.1 nm.

表 S2　本文中四卤化锰(II)配合物的发光波长、寿命和量子效率数据总结

Table S2　The summary of solid emission wavelengths, lifetimes and quantum efficiency of tetrahalomanganese(II) complexes.

Complex	[MPP]$_2$[MnBr$_4$]	[EPP]$_2$[MnBr$_4$]	[TPP]$_2$[MnBr$_4$][24]	[BPP]$_2$[MnBr$_4$]	[BEA]$_2$[MnBr$_4$]	[BPy]$_2$[MnBr$_4$]	[EPP]$_2$[MnCl$_4$]	[BPP]$_2$[MnCl$_4$]
λ_{em}	509 nm	522 nm	522 nm	510 nm	514 nm	510 nm	524 nm	509 nm
Lifetime	260.5 μs	314.0 μs	317.0 μs	298.4 μs	351.5 μs	288.4 μs	0.92 ms	1.95 ms
Quantum efficiency	0.83	0.91	0.98	0.90	0.43	0.38	0.29	0.32

表 S3　配合物$[BPP]_2[MnBr_4]$、$[BEA]_2[MnBr_4]$、$[BPP]_2[MnCl_4]$和$[EPP]_2[MnCl_4]$晶体堆积结构中存在的分子内/分子间 C－H···π 和 C－H···X (X = Br 或 Cl)相互作用

Table S3　The intra- / inter-molecular C－H···π and C－H···X (X = Br or Cl) interactions for manganese (II) complexes $[BPP]_2[MnBr_4]$, $[BEA]_2[MnBr_4]$, $[BPP]_2[MnCl_4]$ and $[EPP]_2[MnCl_4]$.

$[BPP]_2[MnBr_4]$	C－H···π 2.820 Å	C－H···Br 2.965 Å	
	C－H···π 2.880 Å	C－H···Br 2.974 Å	
	C－H···π 2.920 Å	C－H···Br 2.976 Å	
$[BEA]_2[MnBr_4]$	C－H···π2.840 Å	C－H···Br 2.858 Å	C－H···Br 3.018 Å
	C－H···π 2.930 Å	C－H···Br 2.981 Å	C－H···Br 3.005 Å
		C－H···Br 3.008 Å	C－H···Br 2.878 Å
$[BPP]_2[MnCl_4]$	C－H···π 2.850 Å	C－H···Cl 2.734 Å	C－H···Cl 2.590 Å
		C－H···Cl 2.831 Å	C－H···Cl 2.938 Å
		C－H···Cl 2.760 Å	C－H···Cl 2.878 Å
$[EPP]_2[MnCl_4]$	C－H···π 2.990 Å	C－H···Cl 2.903 Å	C－H···Cl 2.860 Å
		C－H···Cl 2.890 Å	C－H···Cl 2.599 Å
		C－H···Cl 2.892 Å	C－H···Cl 2.817 Å
		C－H···Cl 2.931 Å	C－H···Cl 2.846 Å
		C－H···Cl 2.803 Å	C－H···Cl 2.645 Å