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## **Supporting Information**

# Modulating Room Temperature Phosphorescence through Intermolecular Halogen Bonding

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#### Contents

1. Experimental section	2
1.1 General information	2
1.2 Photophysical measurements	2
1.3 Single crystal X-ray diffraction (XRD) data	3
1.4 Theoretical calculations	3
1.5 Synthetic Procedures	4
2. Supplementary Figures and Tables	6
3. References	24

#### **1. Experimental section**

#### **1.1 General information**

All the reagents and solvents used for the synthesis were purchased from Aldrich and Acros companies and used without further purification. The synthesis procedure was presented in Scheme S1. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AVANCE 500 spectrometer at 500 MHz or 125 MHz with tetramethylsilane (TMS) as the internal standard. The MALDI-TOF-MS mass spectra were obtained from an AXIMA-CFRTM plus instrument.

#### **1.2 Photophysical measurements**

UV-vis spectra of solutions were recorded on a Shimadzu UV-3100 Spectrophotometer. Steady-state photoluminescence (PL) spectra, time-resolved emission spectra (TRES) and lifetimes were recorded using FLS980 Spectrometer equipped with a xenon lamp (Xe300) and microsecond flash-lamp (µF920). Low temperature photophysical measurement was carried out with the sample loaded in a quartz tube. Liquid nitrogen was placed into the temperature control attachment for low temperature (77 K). Steady state photoluminescence spectra were measured by an RF-5301PC spectrophotometer. Quantum efficiencies were measured using an integrating sphere apparatus. The excitation wavelengths for PLQY measurements were 300 nm for MPh, MPh-F, MPh-Cl, MPh-Br and MPh-I crystals. Solutions were placed in 1 cm path length quartz cells, and crystals were fixed on the quartz plate in terms of steadystate spectra and lifetimes.

The total lifetimes of multi-sectioned PL-decay spectra are calculated using the following equation:

$$\tau = \frac{\sum_{i=1}^{n} \tau_1^2 A_i}{\sum_{i=1}^{n} \tau_i A_i}$$

where  $\tau$  is the lifetime, *i* represents for the number of the lifetime components, and *Ai* is the proportion for each lifetime components.

#### 1.3 Single crystal X-ray diffraction (XRD) data

Single crystals of MPh, MPh-F, MPh-Cl, MPh-Br and MPh-I were prepared by crystallization from the solution of dichloromethane and petroleum ether at room temperature. The diffraction experiments were carried out on a Rigaku R-AXIS RAPID diffractometer equipped with a Mo-K $\alpha$  and control Software using the RAPID AUTO at 100 K. The crystal structures were solved with direct methods and refined with a full-matrix least-squares technique using the SHELXS programs. Powder XRD patterns were collected on a Rigaku SmartLab (3) diffractometer.

#### **1.4 Theoretical calculations**

All the density functional theory (DFT) calculations were carried out using Gaussian 09 (version D.01) package on a PowerLeader cluster.<sup>1</sup> Single-molecule structures of morpholine derivatives were adopted from optimized single crystal data to calculate vertical excitation energy using time-dependent DFT (TD-DFT) at the level of B3LYP/6-31G(d, p). Spin-orbit coupling (SOC) coefficients were calculated at the level of B3LYP/6-31G(d, p) by Beijing density function (BDF) program. Natural transition orbitals (NTOs) were calculated to identify the excited-state property for both singlet and triplet states.<sup>2-4</sup>

#### **1.5 Synthetic Procedures**



Scheme S1. The synthetic routes of MPh-F, MPh-Cl, MPh-Br and MPh-I.

**MPh** were purchased from Aldrich and Acros companies and purified by column chromatography on silica gel using dichloromethane/petroleum ether (4:1) as the eluent. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  7.30 (t, *J* = 7.7 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.89 (t, *J* = 7.2 Hz, 1H), 3.89 – 3.84 (m, 4H), 3.19 – 3.14 (m, 4H); <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  151.55, 129.07, 119.70, 115.54, 66.88, 49.34; MALDI-TOF MS (mass *m/z*): 163.22. Calcd for C<sub>10</sub>H<sub>13</sub>NO: C 73.59, H 8.03, N 8.58; Found: C 73.53, H 8.03, N 8.61.

Synthesis of **MPh-F**: 1-bromo-4-fluorobenzene (1.75 g, 10 mmol), morpholine (1.04 g, 12 mmol), potassium tert-butoxide (1.12g, 10 mmol),  $[Pd_2(dba)_3]$  (0.27g, 0.3mmol) and tri-tert-butylphosphine tetrafluoroborate (0.14 g, 0.5 mmol) were dissolved in toluene (60 mL). The resultant mixture was refluxed for 24 hours under N<sub>2</sub>, then extracted with dichloromethane. The combined organic extracts were dried over anhydrous MgSO<sub>4</sub> and concentrated by rotary evaporation. The crude product was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (v/v = 6:1) as eluent to afford a white solid in a yield of 57%. <sup>1</sup>H NMR (500 MHz,

CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  7.02 (t, *J* = 8.6 Hz, 1H), 6.92 (s, 1H), 3.86 (d, *J* = 3.9 Hz, 2H), 3.20 – 2.99 (m, 2H). <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  158.04, 148.23, 117.25, 117.20, 115.49, 115.31, 66.83, 50.17. MALDI-TOF MS (mass *m*/*z*): 181.17. Calcd for C<sub>10</sub>H<sub>12</sub>FNO: C 66.28, H 6.68, N 7.73; Found: C 66.32, H 6.67, N 7.71.

Synthesis of **MPh-Cl**: The synthetic procedure for MPh-Cl is similar to that of MPh-F described above. White solid were obtained in 76% yield. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  7.32 – 7.18 (m, 1H), 6.88 (d, *J* = 9.0 Hz, 1H), 3.95 – 3.75 (m, 2H), 3.20 – 3.05 (m, 2H). <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  150.15, 128.88, 124.26, 116.70, 66.70, 49.15. MALDI-TOF MS (mass *m*/*z*): 197.56. Calcd for C<sub>10</sub>H<sub>12</sub>ClNO: C 60.77, H 6.12, N 7.09; Found: C 60.83, H 6.14, N 7.04.

Synthesis of **MPh-Br**: The synthetic procedure for MPh-Br is similar to that of MPh-F described above. White solid were obtained in 84% yield. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  7.50 – 7.26 (m, 1H), 6.84 (d, *J* = 6.4 Hz, 1H), 3.85 (s, 2H), 3.14 (d, *J* = 2.9 Hz, 2H). <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  150.53, 131.80, 117.10, 111.55, 66.67, 48.98. MALDI-TOF MS (mass *m*/*z*): 241.12. Calcd for C<sub>10</sub>H<sub>12</sub>BrNO: C 49.61, H 5.00, N 5.79; Found: C 49.59, H 5.02, N 5.80.

Synthesis of **MPh-I**: The synthetic procedure for MPh-I is similar to that of MPh-F described above. White solid were obtained in 67% yield. <sup>1</sup>H NMR (500 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  7.57 (d, *J* = 8.9 Hz, 1H), 6.75 (d, *J* = 8.7 Hz, 1H), 3.94 – 3.73 (m, 2H), 3.23 – 3.06 (m, 2H). <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  151.05, 150.40, 137.75, 117.54, 81.14, 66.63, 48.75. MALDI-TOF MS (mass *m/z*): 289.24. Calcd for C<sub>10</sub>H<sub>12</sub>INO: C 41.54, H 4.18, N 4.84; Found: C 41.57, H 4.20, N 4.82.

#### 2. Supplementary Figures and Tables



Figure S2. The  ${}^{13}C$  NMR spectrum of MPh in  $CD_2Cl_2$ .



Figure S3. The <sup>1</sup>H NMR spectrum of MPh-F in  $CD_2Cl_2$ .



Figure S4. The  ${}^{13}C$  NMR spectrum of MPh-F in CD<sub>2</sub>Cl<sub>2</sub>.



Figure S5. The <sup>1</sup>H NMR spectrum of MPh-Cl in CD<sub>2</sub>Cl<sub>2</sub>.



Figure S6. The <sup>13</sup>C NMR spectrum of MPh-Cl in CD<sub>2</sub>Cl<sub>2</sub>.



Figure S7. The <sup>1</sup>H NMR spectrum of MPh-Br in CD<sub>2</sub>Cl<sub>2</sub>.



Figure S8. The  ${}^{13}$ C NMR spectrum of MPh-Br in CD<sub>2</sub>Cl<sub>2</sub>.



Figure S10. The  ${}^{13}C$  NMR spectrum of MPh-I in  $CD_2Cl_2$ .



Figure S11. UV/vis absorption of MPh, MPh-F, MPh-Cl, MPh-Br and MPh-I in tetrahydrofuran solution  $(10^{-5} \text{ M})$ .



**Figure S12.** Fluorescence spectra of (a) MPh, (b) MPh-F, (c) MPh-Cl, (d) MPh-Br and (e) MPh-I in various solvents (10<sup>-5</sup> M).



**Figure S13.** The normalized phosphorescence spectra (delayed 10 ms) of MPh, MPh-F, MPh-Cl, MPh-Br and MPh-I in THF solution  $(10^{-5} \text{ M})$  at 77K.



**Figure S14.** The normalized photoluminescence spectra of MPh, MPh-Cl, MPh-Br and MPh-I in THF solution (10<sup>-5</sup> M) at 77K.



**Figure S15.** The normalized photoluminescence spectra of MPh, MPh-Cl, MPh-Br and MPh-I in crystals at 77K.



Figure S16. XRD patterns in different states for MPh, MPh-Cl, MPh-Br and MPh-I.



**Figure S17.** Phosphorescence lifetime of (a) MPh, (b) MPh-Cl, (c) MPh-Br and (d) MPh-I before and after being ground at room temperature.



Figure S18. Intermolecular interactions in crystal and related dimers of MPh.



Figure S19. Intermolecular interactions in crystal and related dimers of MPh-F.



Figure S20. Intermolecular interactions in crystal and related dimers of MPh-Cl.



Figure S21. Intermolecular interactions in crystal and related dimers of MPh-Br.



Figure S22. Intermolecular interactions in crystal and related dimers of MPh-I.



**Figure S23.** Calculated excitation energies, spin-orbit couplings ( $\xi$ ) for MPh and MPh-Cl as coupled units.



**Figure S24.** Calculated excitation energies, spin-orbit couplings ( $\xi$ ) for MPh-F as isolated states and coupled units.



**Figure S25.** Different electrostatic potential analysis of MPh, MPh-F, MPh-Cl, MPh-Br and MPh-I. The potential energy range is -0.03 to 0.03 H.  $q^{-1}$  for all surfaces shown.



Figure S26. High-performance liquid chromatogram spectra. HPLC of MPh, MPh-F, MPh-Cl, MPh-Br and MPh-I in acetonitrile solution (50  $\mu$ M).

Table S1. Emission lifetimes of MPh,	MPh-F, MPh-Cl, MPh-Br	and MPh-I in crystals
under ambient conditions.		

Com		Fluorescence					Phosphorescence				
d d	λ <sub>em</sub> / nm	$\tau_1/$ ns	$A_1 / \%$	$\tau_2/$ ns	$A_2 / \%$	$\tau_l/ms$	$A_1 / \%$	$\tau_2/ms$	$A_2 / \%$	$\tau_3/ms$	A <sub>3</sub> / %
MPh	345	1.96	98.94	3.54	1.06	-	-	-	-	-	-
1411 11	504	-	-	-	-	49.52	3.18	302.70	56.31	575.80	40.52
MPh -F	355	2.02	80.52	4.65	19.48	-	-	-	-	-	-
MPh	367	0.63	51.61	2.92	48.39	-	-	-	-	-	-
-Cl	495	-	-	-	-	24.52	1.65	144.30	31.78	228.40	66.57
MPh	360	2.54	79.62	5.37	20.38	-	-	-	-	-	-
-Br	505	-	-	-	-	4.29	13.00	11.11	87.00	-	-
MPh	362	0.96	19.05	3.82	80.95	-	-	-	-	-	-
-I	529	-	-	-	-	0.54	25.61	2.75	74.39	-	-

MPh	Number	d / Å
С-Нπ	2	2.790
	2	2.807
	2	2.883
С-НО	2	2.456

**Table S2.** The intermolecular interactions in MPh crystal.

 Table S3. The intermolecular interactions in MPh-F crystal.

MPh-F	Number	d / Å
С-Нл	2	2.879
С-НО	2	2.437
	2	2.659
C-HF	2	2.554

MPh-Cl	Number	d / Å
С-Нπ	2	2.866
	2	2.871
	2	2.897
C-C1O	2	3.124

 Table S4. The intermolecular interactions in MPh-Cl crystal.

 Table S5. The intermolecular interactions in MPh-Br crystal.

MPh-Br	Number	d / Å
С-Нπ	1	2.831
	2	2.834
C-BrO	2	3.052

 Table S6. The intermolecular interactions in MPh-I crystal.

MPh-I	Number	d / Å			
С-Нπ	1	2.805			
	1	2.834			
C-I0	2	2.990			

Name	MPh	MPh-F	MPh-Cl	MPh-Br	MPh-I
Formula	C <sub>10</sub> H <sub>13</sub> NO	C <sub>10</sub> H <sub>12</sub> FNO	C <sub>10</sub> H <sub>12</sub> ClNO	C <sub>10</sub> H <sub>12</sub> BrNO	C <sub>10</sub> H <sub>12</sub> INO
Wavelength(Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Space Group	C 1 c 1	P 1 21/c 1	P 1 c 1	P 1 c 1	P -1
Cell Lengths(Å)	10.4456(6)	8.8800(7)	9.885(3)	9.9421(7)	5.0417(7)
	11.3777(6)	10.1316(7)	10.023(4)	10.1035(8)	8.8995(11)
	8.1400(4)	10.6588(9)	10.661(4)	10.6866(8)	11.5534(14)
Cell Angles(°)	90	90.00	90.00	90	77.659(5)
	114.871(2)	112.843(2)	110.207(10)	109.715(3)	83.631(5)
	90	90	90	90	89.288(5)
Cell	877.69(8)	883.75(12)	991.3(6)	1010.54(13)	503.25(11)
Volume(Å <sup>3</sup> )					
Z	4	4	4	4	2
Density(g/cm <sup>3</sup> )	1.235	1.362	1.324	1.591	1.908
F(000)	352	384	416	488	280
h <sub>max</sub> ,k <sub>max</sub> ,I <sub>max</sub>	13,14,10	11,12,13	12,12,13	12,13,13	7,13,18
$T_{min}, T_{max}$	0.990,	0.988,	0.960,	0.509,	0.584,
	0.992	0.990	0.966	0.746	0.747
CCDC number	2214385	2224489	2224503	2224534	2224504

**Table S7.** Crystallographic data for MPh, MPh-F, MPh-Cl, MPh-Br and MPh-I.

ci ystais ui	crystals under amotent conditions.								
Compou	$<\tau>_F$	$\Phi_{\rm F}$	$k_r^{\ F}$	$k_{nr}^{\  \  F}$	$<\tau>_P$	$\Phi_{\mathrm{P}}$	$k_r^{P}$	$k_{nr}^{P}$	k <sub>ISC</sub>
compou	[ns]	[%]	[×10 <sup>7</sup>	[×10 <sup>8</sup>	[ms]	[%]	[×10 <sup>-1</sup>	[s <sup>-1</sup> ]	[×10 <sup>8</sup>
na			s <sup>-1</sup> ]	s <sup>-1</sup> ]			s <sup>-1</sup> ]		s <sup>-1</sup> ]
MPh	1.99	11.57	5.79	4.40	458.91	0.6	0.14	2.45	4.43
MPh-F	2.54	11.21	4.41	3.49	-	-	-	-	-
MPh-Cl	2.49	11.95	4.79	3.26	208.53	6.8	3.67	5.03	3.53
MPh-Br	3.12	6.88	2.20	2.84	10.73	4.2	42.03	95.87	2.98
MPh-I	3.28	5.28	1.61	2.81	2.60	2.3	93.39	396.71	2.88

**Table S8.** Photophysical parameters of MPh, MPh-F, MPh-Cl, MPh-Br and MPh-I in crystals under ambient conditions.<sup>5-6</sup>

 $\begin{aligned} k_r^{P} &= \Phi_P \ / \ < \!\!\tau \!\!>_P \!\!\Phi_{ISC}, \ k_{nr}^{P} = (1 - \Phi_P) \ / \ < \!\!\tau \!\!>_P \!\!\Phi_{ISC}, \ k_r^{F} = \Phi_F \ / \ < \!\!\tau \!\!>_F, \ k_{nr}^{F} = (1 - \Phi_F - \Phi_P) \ / \ < \!\!\tau \!\!>_F, \\ k_{ISC} &= \Phi_{ISC} \ / \ < \!\!\tau \!\!>_F, \ \Phi_{ISC} \!= \!\!1 - \Phi_F \end{aligned}$ 

MPh	Monomer	Dimer
S <sub>0</sub> /T <sub>1</sub>	1.159	1.150
$S_1/T_1$	1.739	1.770
$S_{1}/T_{2}$	0.868	0.131
S <sub>1</sub> /T <sub>3</sub>	0.987	0.836
$S_1/T_4$	0.387	0.290
$S_{1}/T_{5}$	1.354	0.966
$S_1/T_6$	0.672	0.007
$S_{1}/T_{7}$	0.752	0.334
$S_{1}/T_{8}$	0.480	0.032
$S_{1}/T_{9}$	1.208	0.049
S <sub>1</sub> /T <sub>10</sub>	0.024	0.060

**Table S9.** Spin-orbit coupling (SOC) values of MPh for the monomer and dimer.

MPh-Cl	Monomer	Dimer
S <sub>0</sub> /T <sub>1</sub>	2.637	2.679
$S_1/T_1$	2.580	2.584
$S_{1}/T_{2}$	1.129	0.753
S <sub>1</sub> /T <sub>3</sub>	2.986	1.149
$S_1/T_4$	0.381	0.164
$S_{1}/T_{5}$	0.855	2.979
$S_1/T_6$	1.064	0.031
$S_{1}/T_{7}$	0.500	0.388
$S_{1}/T_{8}$	0.459	0.252
$S_{1}/T_{9}$	0.024	0.001
S <sub>1</sub> /T <sub>10</sub>	0.006	0.045

 Table S10. Spin-orbit coupling (SOC) values of MPh-Cl for the monomer and dimer.

MPh-F	Monomer	Dimer
S <sub>0</sub> /T <sub>1</sub>	1.512	0.000
$S_1/T_1$	0.537	0.000
$S_{1}/T_{2}$	2.015	1.640
S <sub>1</sub> /T <sub>3</sub>	0.847	0.001
$S_1/T_4$	1.044	0.997
S <sub>1</sub> /T <sub>5</sub>	0.449	0.254
$S_1/T_6$	0.916	0.000
$S_{1}/T_{7}$	0.768	0.000
S <sub>1</sub> /T <sub>8</sub>	0.278	0.001
$S_{1}/T_{9}$	0.881	0.016
S <sub>1</sub> /T <sub>10</sub>	0.042	0.000

**Table S11.** Spin-orbit coupling (SOC) values of MPh-F for the monomer and dimer.

### 3. References

- R. Gaussian, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, G. Scalmani, V. Barone, B. Mennuci, G. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. Hratchian, A. Izmaylov, J. Bloino, G. Zheng, J. Sonnenberg, M. Hada and D. Fox, *Gaussian, Inc., Wallingford CT*, 2004.
- 2. W. Liu, F. Wang and L. Li, J. Theor. Comput. Chem., 2003, 2, 257-272.
- 3. Z. Li, Y. Xiao and W. Liu, J. Chem. Phys., 2012, 137, 154114.
- 4. Li, B. Suo, Y. Zhang, Y. Xiao and W. Liu, Mol. Phys., 2013, 111, 3741-3755.
- 5. S. Hirata, Applied Physics Reviews, 2022, 9, 011304.

 W. Zhao, T. S. Cheung, N. Jiang, W. Huang, J. W. Y. Lam, X. Zhang, Z. He and B. Z. Tang, *Nat. Commun.*, 2019, **10**, 1595.