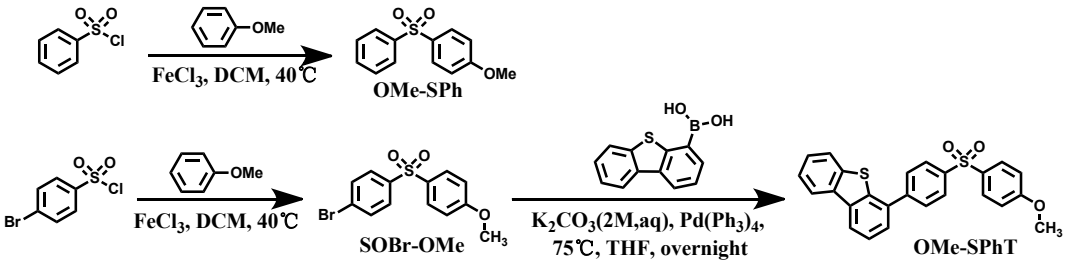
# Supporting Information

## 1 Synthesis and Characterization of Compounds

**Materials.** Sulfobenzide, 4-bromobenzene-1-sulfonyl chloride, anisole, benzenesulfonyl chloride，and dibenzo[b,d]thiophen-4-ylboronic acid were purchased from Aldrich. And sulfobenzide was further purified to use in experiment. Potassium *tert*-butoxide was purchased from Alfa Aesar. The other reagents were purchased from Aladdin Industrial.

**Characterization.** $^1$H NMR spectra were obtained from a Varian Mercury-Plus 500 Nuclear Magnetic Resonance Spectrometer in $CDCl_3$, using tetramethylsilane (TMS) as the internal standard. High-resolution EI mass spectra were performed with on a MAT95XP-HRM spectrometer. Using Hitachi U-3900 spectrophotometer to measure the UV-visible absorption spectra of the final compounds. The steady-state emission and persistent phosphorescence emission were carried out with a Shimadzu RF-5301 PC spectrometer or an Ocean Optics Maya Pro2000 with 310 nm and 365 nm Rhinospectrum RhinoLED as the excitation source. Wide-angle X-ray diffraction (XRD) measurements were performed at 293 K using an X-ray diffractometer (Smartlab, Rigaku Co.) with an X-ray source of Cu Kα (λ= 0.15406 nm) at 40 kV and 30 mA at a scan rate of 4° (2θ)/min. The temperature-dependent emission studies were measured on Horiba JY FL-3 spectrometer equipped with a calibrated integrating sphere. Single-crystal analyses of SPh, OMe-SPh and OMe-SPhT were attained through an Oxford Diffraction Gemini S Ultra X-ray Single Crystal Diffractometer with a (Cu) X-ray source. The TD-DFT calculations were performed at the rb3lyp/6-31g(d) level in the Gaussian 09 software.

**Synthetic Routes:**




**Scheme S1** Synthetic routes for OMe-SPh and OMe-SPhT compounds.

**Synthetic Details:**

Sulfobenzide (SPh) was purchased from Aldrich immediately and further recrystallized using the solvent of dichloromethane and n-hexane. The intermediate compounds (SOBr-OMe) and the final compounds of OMe-SPh and OMe-SPhT were synthesized according to our previous work,[1] except that the dibenzo[b,d]furan-4-ylboronic acid was replaced by dibenzo[b,d] thiophene -4-ylboronic acid.

**Sulfobenzide (SPh)** $^{1}$H NMR (500 MHz, $CDCl_3$, 298K): δ = 7.98-7.93 (m, 4H), 7.59-7.54 (m, 2H), 7.52-7.49 (m, 4H); $^{13}$C NMR (DMSO): δ 141.57, 134.19, 130.23, 127.80. High Resolution EI-MS: m/z found: 218.0397 $[M]^+$; calcd for $C_{12}H_{10}O_2S$: 218.0402.

**1-methoxy-4-(phenylsulfonyl)benzene (OMe-SPh)** A white solid was achieved. Yield: 1.78 g (63.3 %). $^{1}$H NMR (500 MHz, $CDCl_3$, 298K): δ = 7.92 (d, 8.0Hz, 2H), 7.88 (d, 8.5 Hz, 2H), 7.57-7.45 (m, 3H), 7.00-6.93 (m, 2H), 3.84 (s, 3H); $^{13}$C NMR (DMSO): δ 163.59, 142.41, 133.78, 133.01, 133.01, 130.15, 127.42, 115.42. High Resolution EI-MS: m/z found: 248.0501 $[M]^+$; calcd for $C_{13}H_{12}O_3S$: 248.0507.

**4-(4-((4-methoxyphenyl)sulfonyl)phenyl)dibenzo[b,d]thiophene (OMe-SPhT)**

A white solid was achieved. Yield: 1.31 g (85.5 %). $^{1}$H NMR (500 MHz, $CDCl_3$, 298K): δ = 8.23-8.17 (m, 2H), 8.05 (d, 8.5 Hz, 2H), 7.96 (d, 9Hz, 2H), 7.98-7.80 (m, 3H), 7.60-7.54 (m, 1H), 7.52-7.42 (m, 3H), 7.05-6.99 (m, 2H), 3.89-3.85 (s, 3H); $^{13}$C NMR (DMSO): δ 163.77, 144.88, 141.97, 138.63, 137.67, 136.49, 135.51, 134.87, 133.82, 130.32, 129.69, 128.22, 127.93, 127.85, 126.23, 125.49, 123.35, 122.82, 122.59, 115.57, 56.31. High Resolution EI-MS: m/z found: 430.0694 $[M]^+$; calcd for $C_{25}H_{18}O_3S_2$: 430.0697.

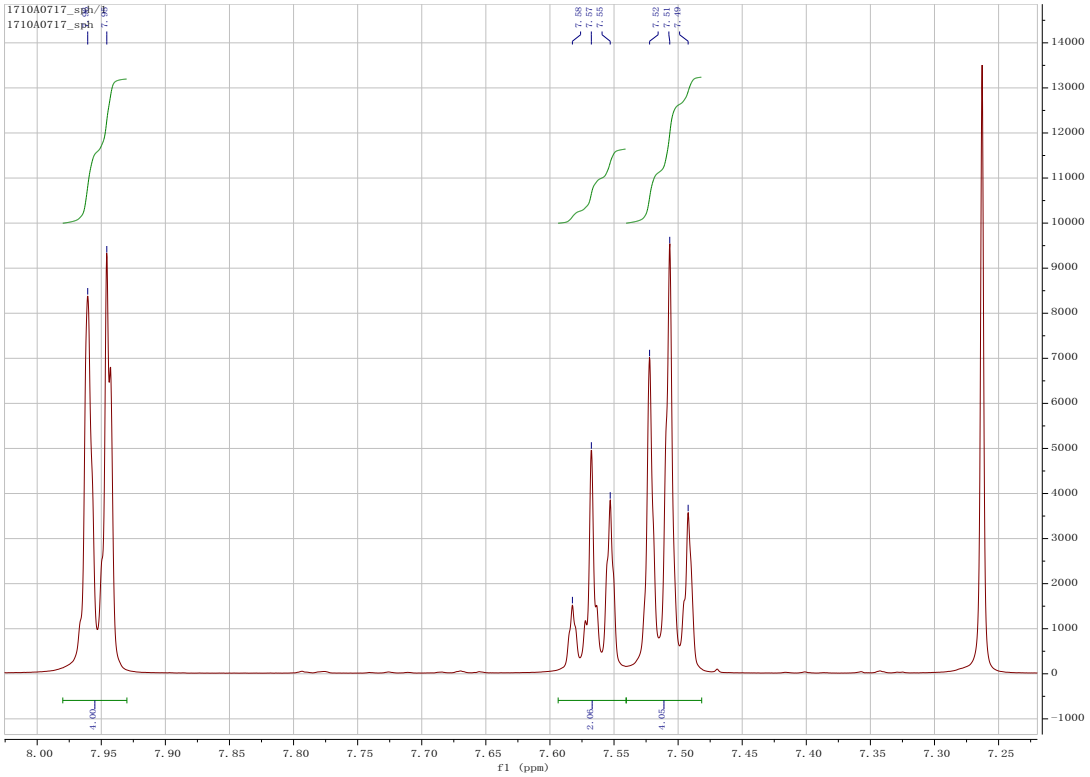



**Figure S1.** The $^{1}$H NMR spectrum of of SPh.

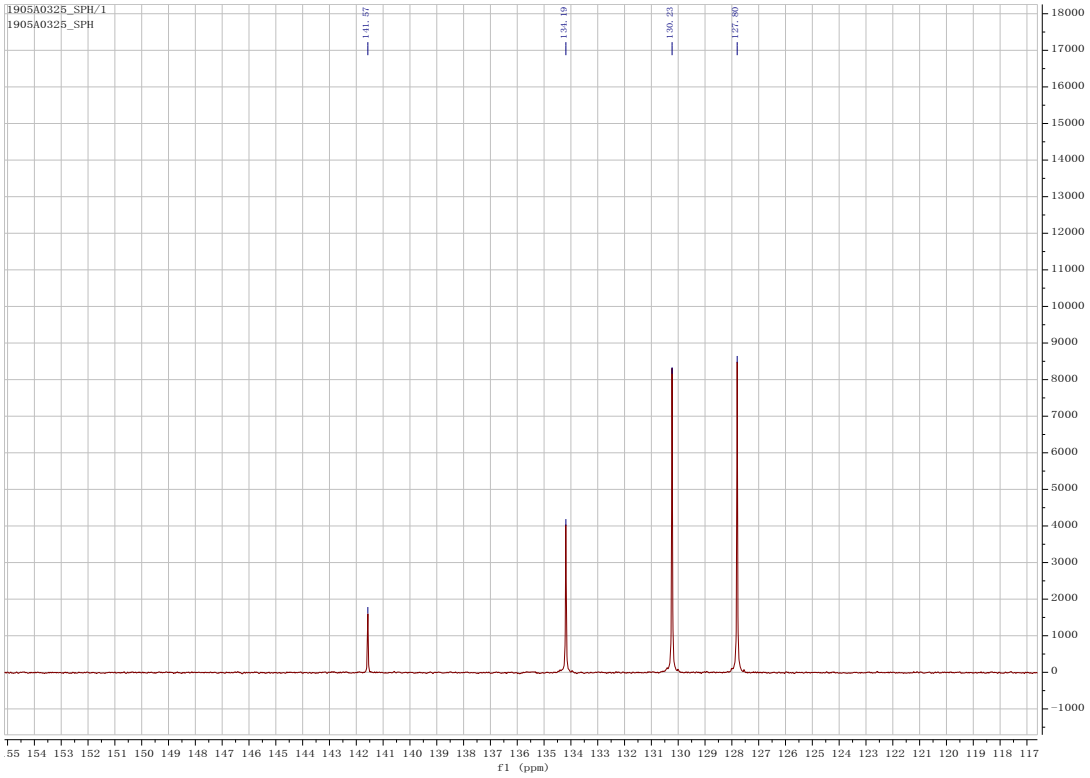



**Figure S2.** The $^{13}C$ NMR spectrum of of SPh.

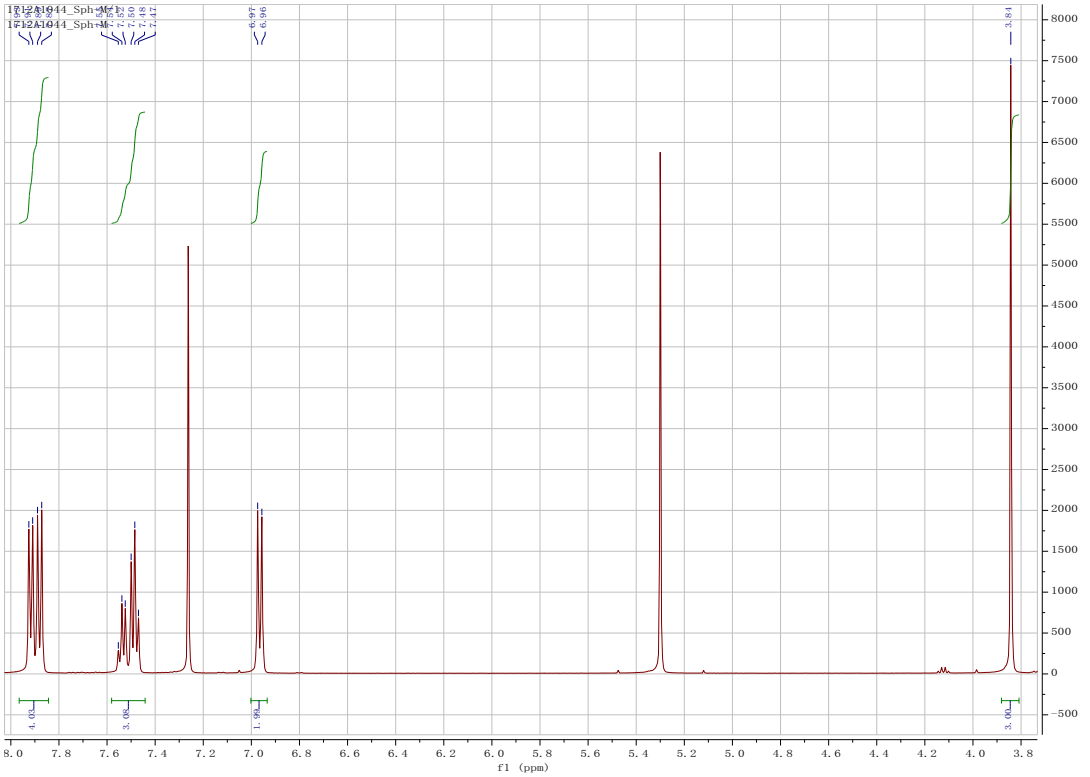



**Figure S3.** The $^{1}H$ NMR spectrum of of OMe-SPh.

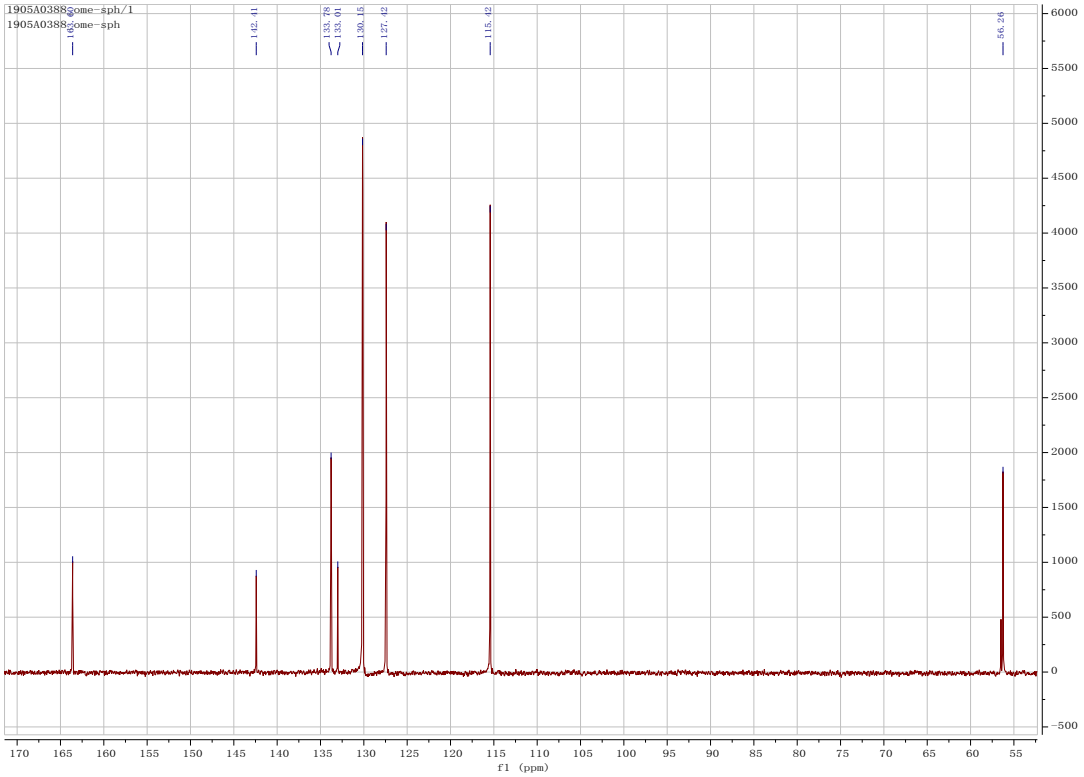



**Figure S4.** The $^{13}C$ NMR spectrum of of OMe-SPh.

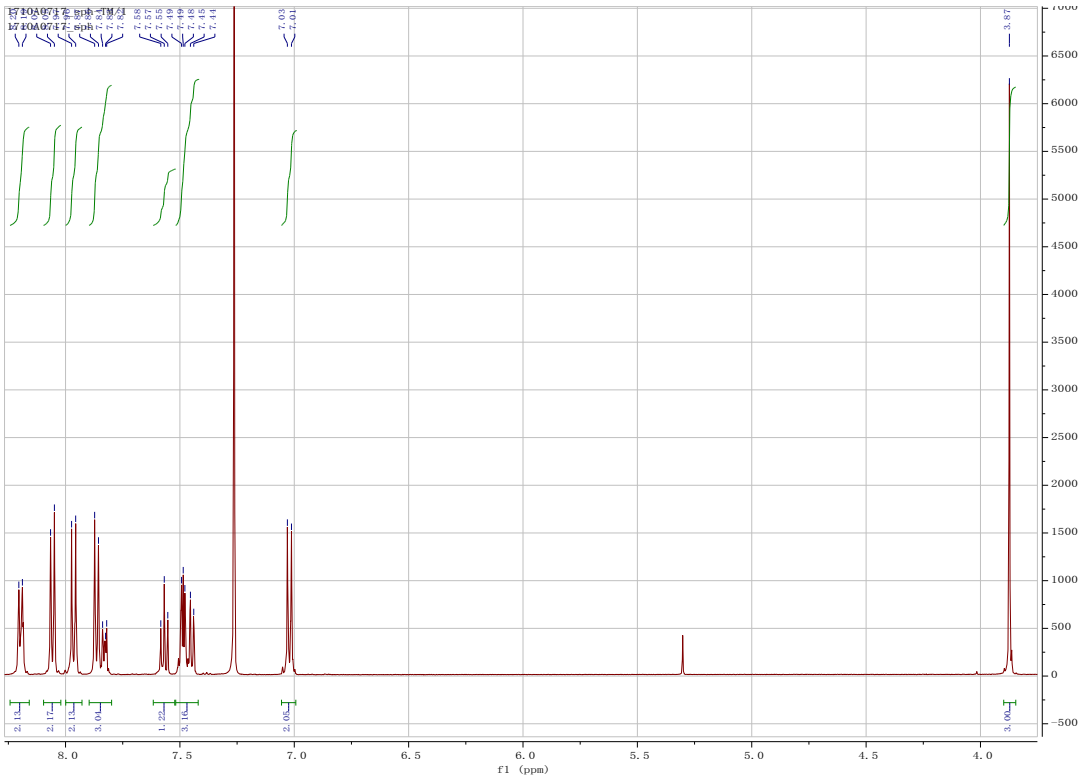



**Figure S5.** The $^{1}H$ NMR spectrum of of OMe-SPhT

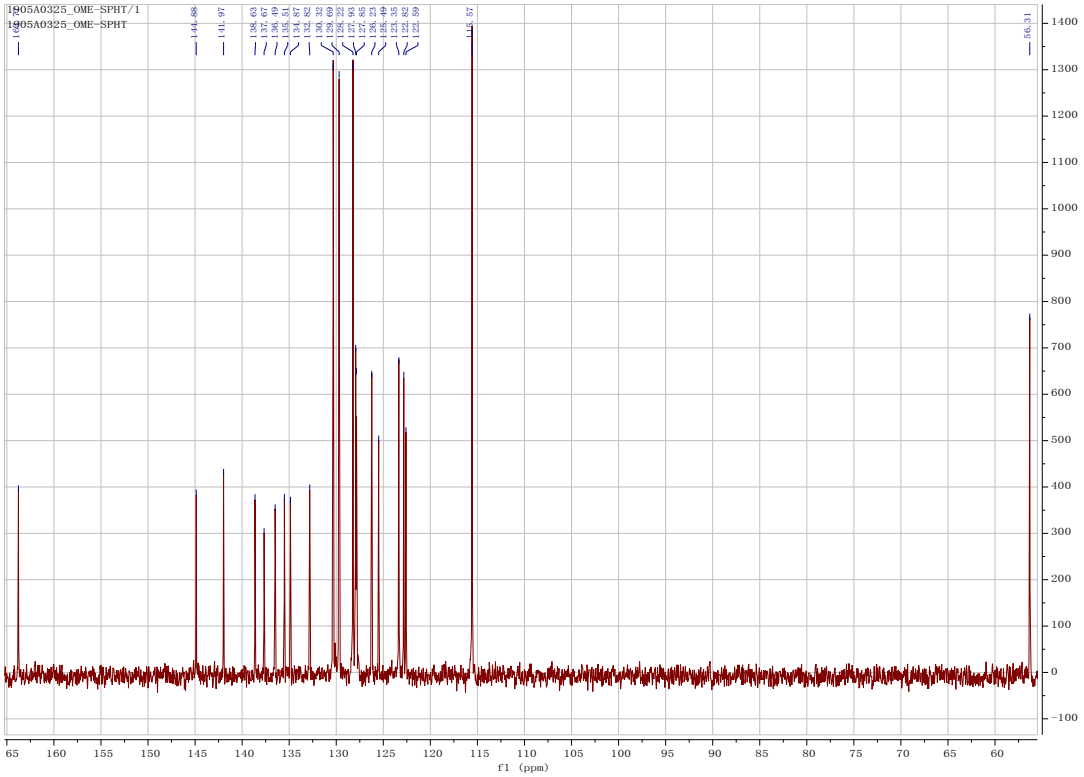



**Figure S6.** The $^{13}$C NMR spectrum of of OMe-SPhT

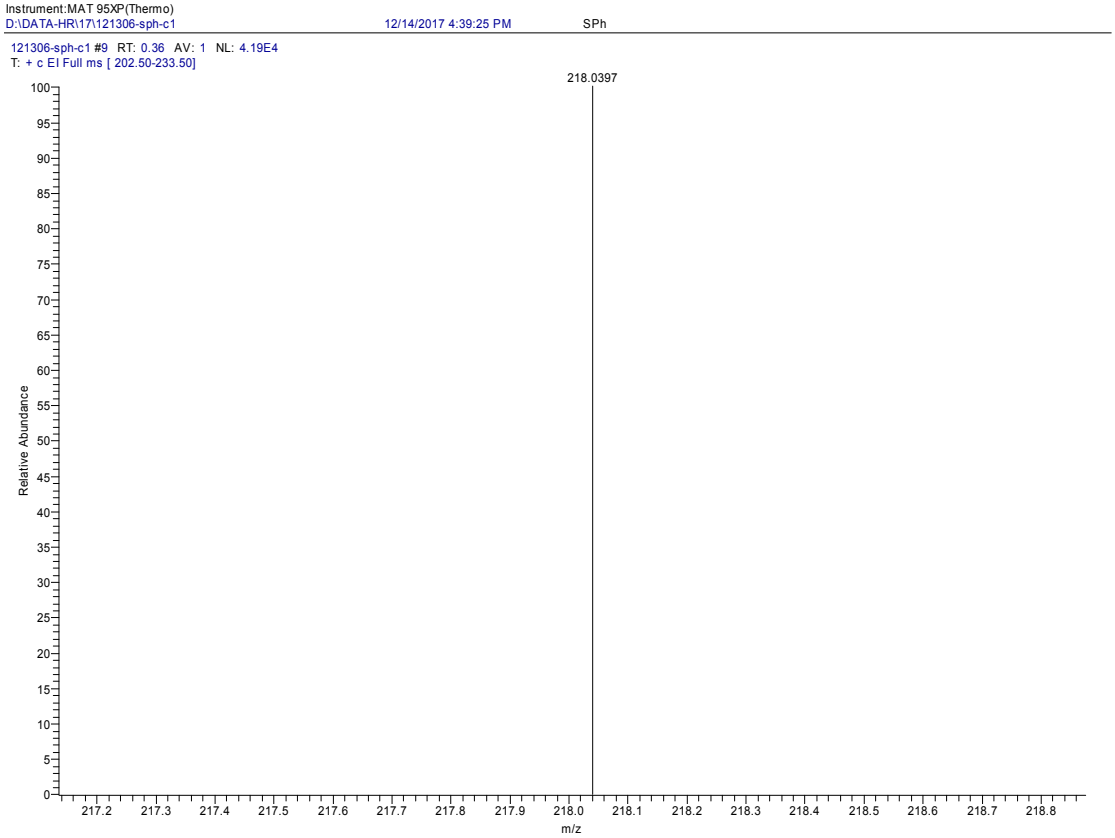



**Figure S7.** High-resolution EI mass spectrum of SPh

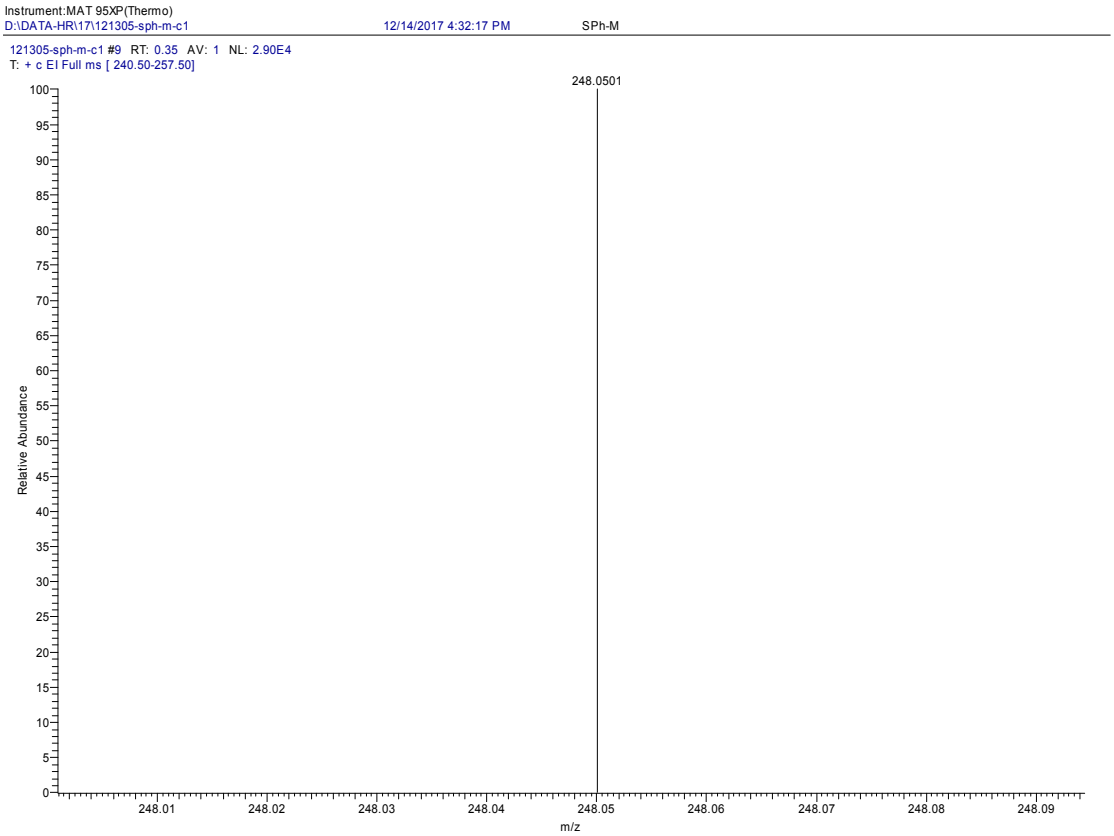



**Figure S8.** High-resolution EI mass spectrum of OMe-SPh

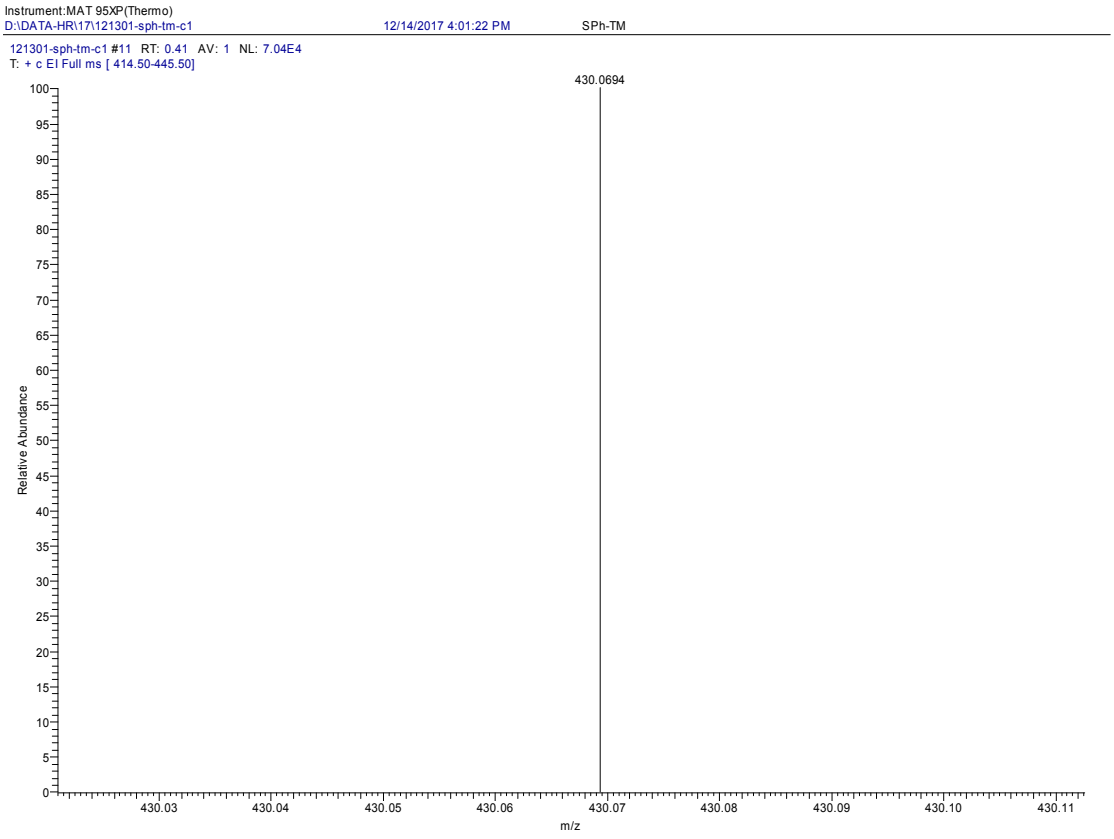



**Figure S9.** High-resolution EI mass spectrum of OMe-SPhT

## 2 Single crystal data of SPh, OMe-SPh and OMe-SPhT

Single-crystal X-ray data of SPh, OMe-SPh and OMe-SPhT were collected by an Oxford Diffraction Gemini S Ultra X-ray Single Crystal Diffractometer with a (Cu) X-ray source. The single-crystal structures were solved by Olex2 v1.2 program and expanded using Fourier techniques. All non-H atoms of the compounds were refined with anisotropic thermal parameters. The hydrogen atoms were added in idealized positions and refined with fixed geometry according to their carrier atoms. CCDC numbers for the single-crystal structures of SPh, OMe-SPh and OMe-SPhT are 1905615, 1834499 and 1835838 respectively.

Crystal Data for SPh: $C_{12}H_{10}O_2S$ (M =218.26 g/mol), monoclinic, space group $P2_1/c$, a = 12.0982(2) Å, b = 7.66810(10) Å, c = 11.24180(10) Å, α=90° β = 96.7340(10)°, γ=90°, V = 1035.71(2) $Å^3$, Z = 4, T = 150.00(10) K, μ(CuKα) = 2.573 $mm^{-1}$, $\rho_c$ = 1.400 $g/cm^3$, Reflections collected 15305, Independent reflections 2084 unique ($R_{int}$ = 0.0449, $R_{sigma}$ = 0.0225). $R_1$ = 0.0309 (I > 2σ (I)) and $wR_2$ = 0.0833 (all data). GOF = 1.083.

Crystal Data for OMe-SPh: $C_{13}H_{12}O_3S$ (M =248.29 g/mol), monoclinic, space group $P2_1/n$, a = 13.9202(7) Å, b = 8.0462(4) Å, c = 11.3730(5) Å, α=90°, β = 105.687(5)°, γ=90°, V = 1226.38(4) $Å^3$, Z = 4, T = 290.00(10) K, μ(CuKα) = 2.302 $mm^{-1}$, $\rho_c$ = 1.345 $g/cm^3$, Reflections collected 3483, Independent reflections 2335 unique ($R_{int}$ = 0.0233, $R_{sigma}$ = 0.0269). $R_1$= 0.0478 (I>=2σ (I)) and $wR_2$ = 0.1597 (all data). GOF = 1.156.

Crystal Data for OMe-SPhT: $C_{25}H_{18}O_3S_2$ (M =430.55 g/mol), monoclinic, space group $P2_1/n$, a = 7.1560(18) Å, b = 7.9129(18) Å, c = 35.708(10) Å, α=90°, β = 91.70(2)°, γ=90°, V = 2021.1(9) $Å^3$, Z = 4, T = 290.00(10) K, μ(CuKα) = 2.595 $mm^{-1}$, $\rho_c$ = 1.4149 $g/cm^3$, Reflections collected 4832, Independent reflections 2967 unique ($R_{int}$ = 0.0238, $R_{sigma}$ = 0.0336). $R_1$= 0.0478 (I>=2u (I)) and $wR_2$ = 0.0903 (all data).

GOF = 1.054.

***Table S1***. Bond distances (Å) for SPh

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| S1 | C1 | 1.7706(14) | C5 | C6 | 1.384(2) |
| S1 | C2 | 1.7660(13) | C5 | C12 | 1.388(2) |
| S1 | O3 | 1.4411(11) | C6 | C10 | 1.388(2) |
| S1 | O4 | 1.4406(11) | C7 | C8 | 1.385(2) |
| C1 | C11 | 1.3898(19) | C7 | C13 | 1.385(2) |
| C1 | C12 | 1.3879(19) | C9 | C14 | 1.388(2) |
| C2 | C8 | 1.3917(18) | C10 | C11 | 1.384(2) |
| C2 | C9 | 1.3910(19) | C13 | C14 | 1.386(2) |

***Table S2***. Bond angles for SPh

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C2 | S1 | C1 | 104.32(6) | C9 | C2 | C8 | 119.8(2) |
| O3 | S1 | C1 | 108.27(6) | C6 | C5 | C12 | 119.8(3) |
| O3 | S1 | C2 | 108.30(6) | C5 | C6 | C10 | 120.3(3) |
| O4 | S1 | C1 | 107.61(6) | C8 | C7 | C13 | 119.5(3) |
| O4 | S1 | C2 | 108.23(6) | C7 | C8 | C2 | 120.8(3) |
| O4 | S1 | O3 | 119.13(7) | C14 | C9 | C2 | 119.5(3) |
| C11 | C1 | S1 | 119.24(10) | C11 | C10 | C6 | 120.7(3) |
| C12 | C1 | S1 | 119.11(10) | C10 | C11 | C1 | 118.5(3) |
| C12 | C1 | C11 | 121.65(13) | C5 | C12 | C1 | 119.2(3) |
| C8 | C2 | S1 | 119.40(10) | C7 | C13 | C14 | 120.1(3) |
| C9 | C2 | S1 | 118.94(10) | C13 | C14 | C9 | 121.0(3) |

***Table S3***. Bond distances (Å) for OMe-SPh

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| S001 | O003 | 1.434(3) | C006 | C00B | 1.392(5) |
| S001 | O004 | 1.439(3) | C007 | C009 | 1.376(4) |
| S001 | C005 | 1.769(3) | C007 | C00A | 1.396(4) |
| S001 | C007 | 1.753(3) | C008 | C009 | 1.378(4) |
| O002 | C006 | 1.349(4) | C00A | C00B | 1.369(4) |

| | | | | | |
|---|---|---|---|---|---|
| O002 | C00H | 1.430(4) | C00C | C00F | 1.378(5) |
| C005 | C00C | 1.378(4) | C00D | C00G | 1.381(5) |
| C005 | C00D | 1.372(4) | C00E | C00F | 1.362(5) |
| C006 | C008 | 1.388(4) | C00E | C00G | 1.369(5) |

***Table S4***. Bond angles for OMe-SPh

| **Atom** | **Atom** | **Atom** | **Angle/°** | **Atom** | **Atom** | **Atom** | **Angle/°** |
|---|---|---|---|---|---|---|---|
| O003 | S001 | O004 | 119.36(17) | C009 | C007 | S001 | 119.8(2) |
| O003 | S001 | C005 | 107.72(16) | C009 | C007 | C00A | 119.8(3) |
| O003 | S001 | C007 | 108.26(15) | C00A | C007 | S001 | 120.3(3) |
| O004 | S001 | C005 | 107.62(15) | C009 | C008 | C006 | 119.5(3) |
| O004 | S001 | C007 | 107.87(16) | C007 | C009 | C008 | 120.8(3) |
| C007 | S001 | C005 | 105.12(13) | C00B | C00A | C007 | 119.5(3) |
| C006 | O002 | C00H | 117.6(3) | C00A | C00B | C006 | 120.7(3) |
| C00C | C005 | S001 | 119.6(2) | C005 | C00C | C00F | 118.5(3) |
| C00D | C005 | S001 | 119.2(2) | C005 | C00D | C00G | 119.2(3) |
| C00D | C005 | C00C | 121.2(3) | C00F | C00E | C00G | 120.1(3) |
| O002 | C006 | C008 | 124.5(3) | C00E | C00F | C00C | 121.0(3) |
| O002 | C006 | C00B | 115.9(3) | C00E | C00G | C00D | 120.1(3) |
| C008 | C006 | C00B | 119.6(3) | | | | |

***Table S5***. Bond distances (Å) for OMe-SPhT

| **Atom** | **Atom** | **Length/Å** | **Atom** | **Atom** | **Length/Å** |
|---|---|---|---|---|---|
| S7aa | O2aa | 1.4405(16) | C4aa | C6ba | 1.385(3) |
| S7aa | C3aa | 1.7690(18) | C5aa | C9ba | 1.376(3) |
| S7aa | C5ba | 1.758(2) | C1 | C3ba | 1.390(3) |
| S7aa | O4ca | 1.4394(15) | C1 | C8ba | 1.389(3) |
| S1aa | C0aa | 1.7588(18) | C8aa | C0ba | 1.388(3) |
| S1aa | C0ba | 1.7437(18) | C8aa | C1ca | 1.374(3) |
| O | C6ba | 1.356(2) | C9aa | C3ba | 1.482(2) |
| O | C2 | 1.423(3) | C9aa | C9ba | 1.399(2) |
| C0aa | C1aa | 1.404(2) | C0ba | C2ba | 1.400(3) |
| C0aa | C3ba | 1.397(2) | C1ba | C8ba | 1.371(3) |
| C1aa | C1ba | 1.392(3) | C2ba | C2ca | 1.398(3) |

| | | | | | |
|---|---|---|---|---|---|
| C1aa | C2ba | 1.446(3) | C4ba | C5ba | 1.388(3) |
| C2aa | C6aa | 1.380(2) | C5ba | C3ca | 1.376(3) |
| C2aa | C9aa | 1.394(3) | C6ba | C7ba | 1.384(3) |
| C3aa | C5aa | 1.383(3) | C7ba | C3ca | 1.377(3) |
| C3aa | C6aa | 1.388(3) | C0ca | C1ca | 1.394(3) |
| C4aa | C4ba | 1.367(3) | C0ca | C2ca | 1.370(3) |

***Table S6***. Bond angles for OMe-SPhT

| **Atom** | **Atom** | **Atom** | **Angle/°** | **Atom** | **Atom** | **Atom** | **Angle/°** |
|---|---|---|---|---|---|---|---|
| C3aa | S7aa | O2aa | 106.46(9) | C9ba | C9aa | C3ba | 120.08(15) |
| C5ba | S7aa | O2aa | 107.05(9) | C8aa | C0ba | S1aa | 125.47(16) |
| C5ba | S7aa | C3aa | 109.03(8) | C2ba | C0ba | S1aa | 112.37(13) |
| O4ca | S7aa | O2aa | 119.38(10) | C2ba | C0ba | C8aa | 122.16(17) |
| O4ca | S7aa | C3aa | 107.75(8) | C8ba | C1ba | C1aa | 120.00(17) |
| O4ca | S7aa | C5ba | 106.88(9) | C0ba | C2ba | C1aa | 112.50(15) |
| C0ba | S1aa | C0aa | 91.21(9) | C2ca | C2ba | C1aa | 129.08(18) |
| C2 | O | C6ba | 119.21(18) | C2ca | C2ba | C0ba | 118.41(18) |
| C1aa | C0aa | S1aa | 112.13(13) | C1 | C3ba | C0aa | 116.97(16) |
| C3ba | C0aa | S1aa | 125.86(13) | C9aa | C3ba | C0aa | 121.36(15) |
| C3ba | C0aa | C1aa | 121.95(16) | C9aa | C3ba | C1 | 121.66(16) |
| C1ba | C1aa | C0aa | 118.85(16) | C5ba | C4ba | C4aa | 118.91(18) |
| C2ba | C1aa | C0aa | 111.74(16) | C4ba | C5ba | S7aa | 118.87(15) |
| C2ba | C1aa | C1ba | 129.40(16) | C3ca | C5ba | S7aa | 120.58(14) |
| C9aa | C2aa | C6aa | 121.75(15) | C3ca | C5ba | C4ba | 120.32(18) |
| C5aa | C3aa | S7aa | 119.79(13) | C4aa | C6ba | O | 115.23(16) |
| C6aa | C3aa | S7aa | 119.26(14) | C7ba | C6ba | O | 124.45(19) |
| C6aa | C3aa | C5aa | 120.63(16) | C7ba | C6ba | C4aa | 120.31(18) |
| C6ba | C4aa | C4ba | 120.82(17) | C3ca | C7ba | C6ba | 118.68(19) |
| C9ba | C5aa | C3aa | 120.08(16) | C1ba | C8ba | C1 | 120.47(17) |
| C8ba | C1 | C3ba | 121.75(17) | C9aa | C9ba | C5aa | 120.56(17) |
| C3aa | C6aa | C2aa | 118.74(16) | C2ca | C0ca | C1ca | 121.05(19) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C1ca | C8aa | C0ba | 118.0(2) | C0ca | C1ca | C8aa | 120.8(2) |
| C3ba | C9aa | C2aa | 121.82(15) | C0ca | C2ca | C2ba | 119.5(2) |
| C9ba | C9aa | C2aa | 118.09(16) | C7ba | C3ca | C5ba | 120.92(17) |

## 3 Supplementary Figures

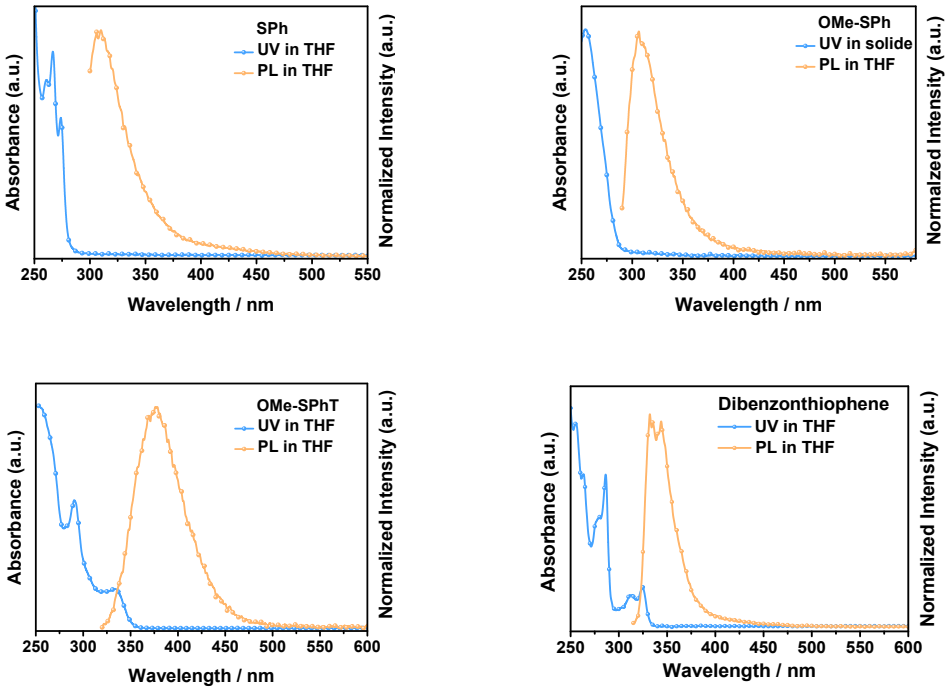



**Figure S10.** UV-vis absorption and emission spectra of SPh, OMe-SPh， OMe-SPhT and dibenzonthiophene in THF solution with a concentration of 1.0 × $10^{-5}$ mol/L.

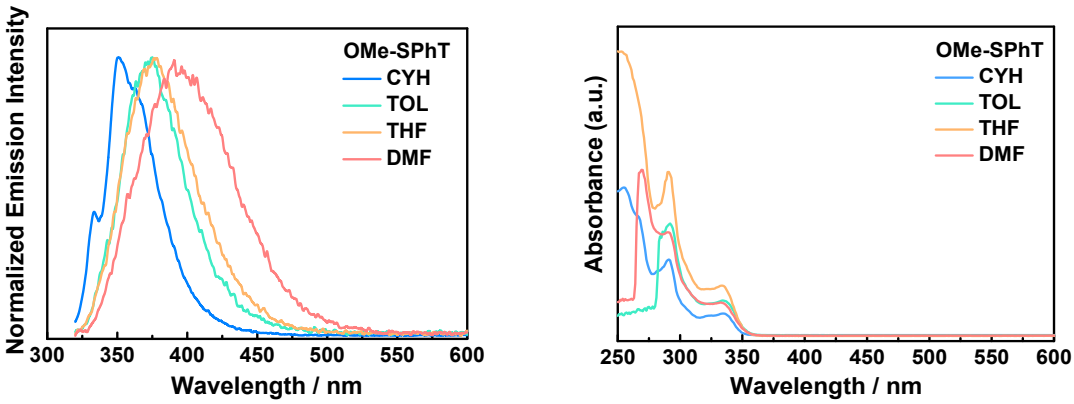



**Figure S11.** UV-vis absorption and emission spectra of OMe-SPhT in different solvents.

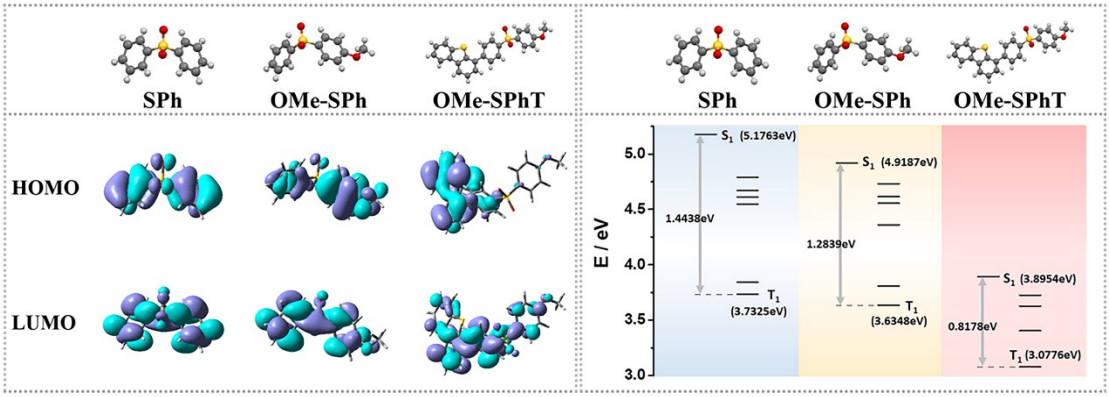



**Figure S12.** Energy level distributions of the isolated molecules simulated in vacuum.

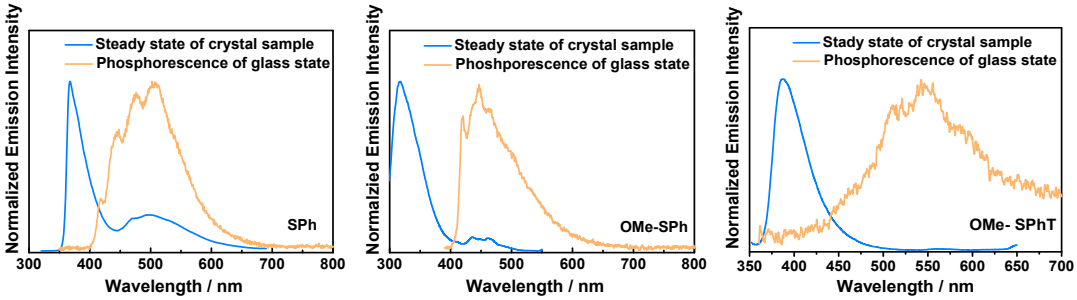



**Figure S13.** Emission spectra of SPh, OMe-SPh and OMe-SPhT in glass state at 77 K (2Me-THF, $1 \times 10^{-5}$ mol/L) and in solid state at 300 K.

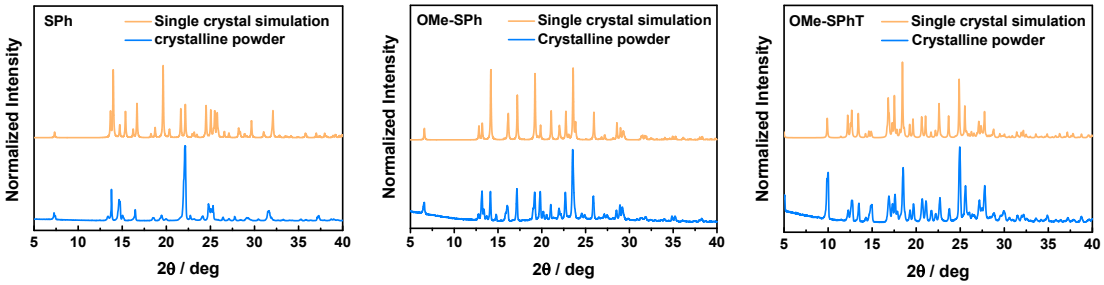



**Figure S14.** PXRD of crystalline powder (SPh, OMe-SPh and OMe-SPhT).

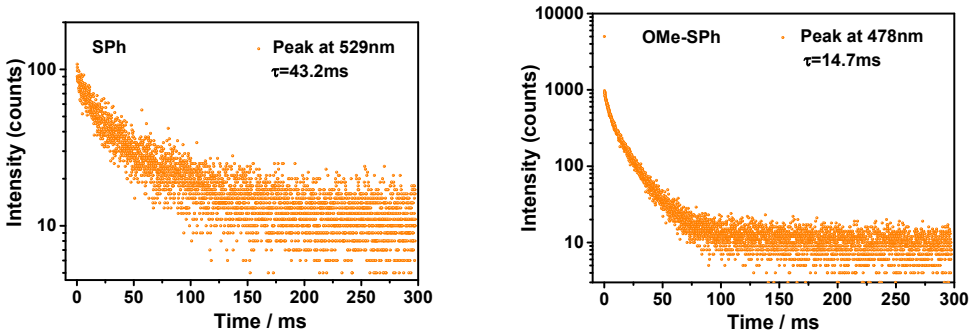



**Figure S15.** Lifetime decay profiles of SPh at 529 nm and OMe-SPh at 478 nm under

ambient conditions.

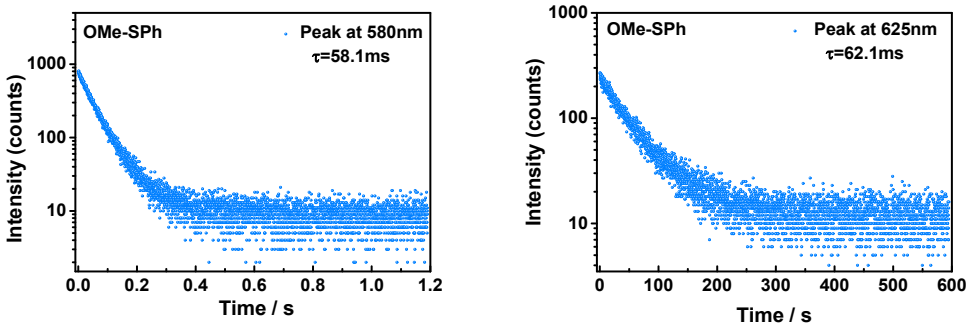



**Figure S16.** Lifetime decay profiles of OMe-SPh at 580 nm and 625 nm under ambient conditions.

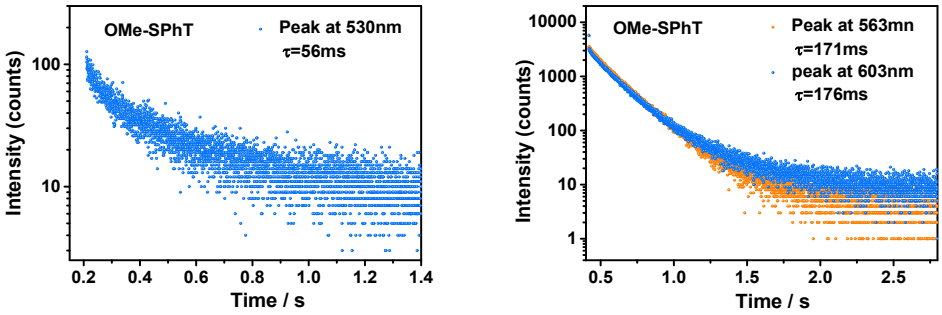



**Figure S17.** Lifetime decay profiles of OMe-SPhT at 530 nm, 563 nm and 603 nm under ambient conditions.

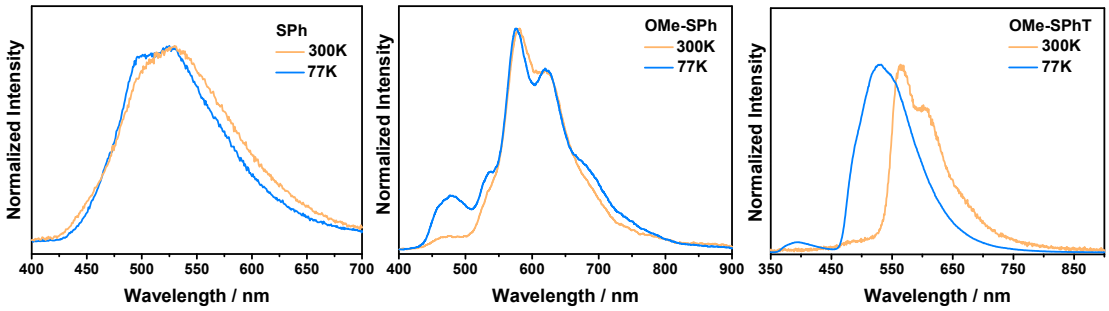



**Figure S18.** Phosphorescence spectra of SPh, OMe-SPh and OMe-SPhT at 300 K and 77 K.

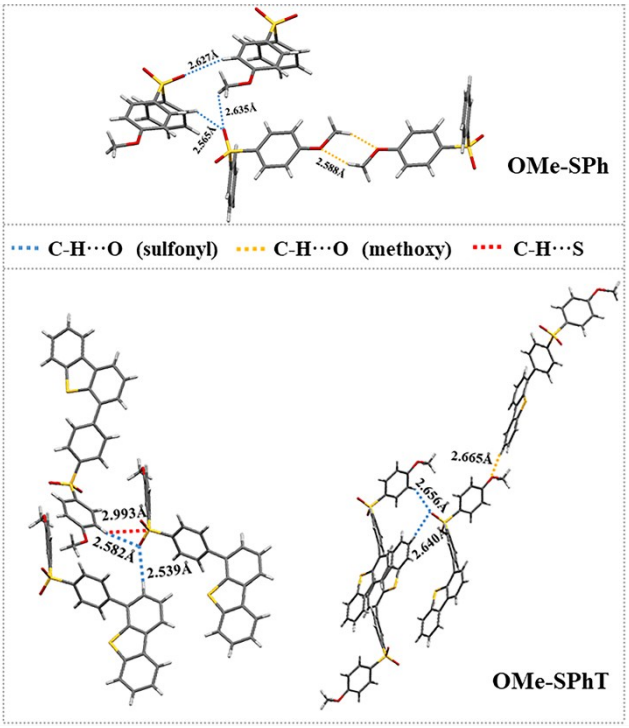



**Figure S19.** The intermolecular interactions in the crystal of OMe-SPh and OMe-SPhT.

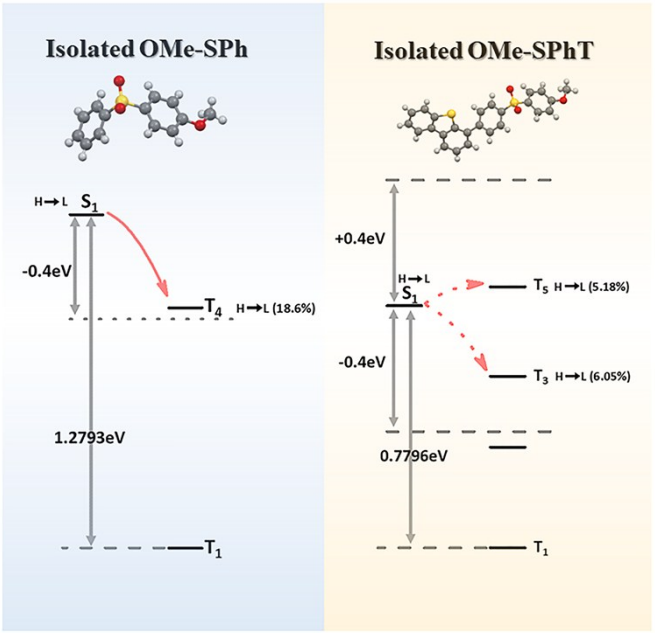



**Figure S20.** The ISC channels between the lowest singlet ($S_1$) and triplet states ($T_n$) of OMe-SPh and OMe-SPhT. (The red solid and dashed arrows represent major and minor ISC channels, respectively)

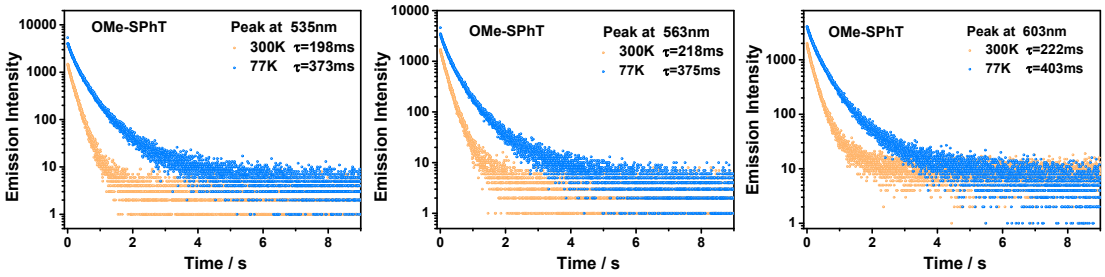



**Figure S21.** Lifetime decay profiles of OMe-SPhT at 535 nm, 563 nm and 603 nm measured at different temperatures.

## Reference

1 J. Chen, T. Yu, E. Ubba, Z. Xie, Z. Yang, Y. Zhang, S. Liu, J. Xu, M. P. Aldred, Z. Chi, *Adv. Opt. Mater.,* 2019, **7**, 1801593.