Supplementary Information

Vapochromic Films of π -Conjugated Polymers Based on Coordination and Desorption at Hypervalent Tin(IV)-Fused Azobenzene Compounds

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General

¹H, ¹³C{¹H} and ¹¹⁹Sn NMR spectra were recorded on JEOL AL400 and ECX400 instruments at 400, 100 and 149 MHz, respectively. Samples were analyzed in CDCl₃. The chemical shift values were expressed relative to Me₄Si for ¹H, ¹³C{¹H} NMR as an internal standard in CDCl₃ and Me₄Sn for ¹¹⁹Sn NMR as a capillary standard. High-resolution mass spectrometry (HRMS) was performed at the Technical Support Office (Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University), and the HRMS spectra were obtained on a Thermo Fisher Scientific EXACTIVE spectrometer for electrospray ionization (ESI) and a Bruker Daltonics ultrafleXtreme for matrix assisted laser desorption ionization (MALDI). UV–vis spectra were recorded on a SHIMADZU UV-3600i Plus spectrophotometer, and samples were analyzed at room temperature. HORIBA JOBIN YVON Fluorolog-3 was used for PL spectra. Absolute photoluminescence quantum efficiency (Φ_{PL}) was recorded on a Hamamatsu Photonics Quantaurus-QY Plus C13534-01. HITACHI HD-1263 TURBO 1200 was used as hair dryer.

Materials

Commercially available compounds used without purification: Diphenyltin(IV) oxide (Sigma-Aldrich Co. LLC.) Dimethyltin(IV) dichloride (FUJIFILM Wako Pure Chemical Corporation) NaOH (FUJIFILM Wako Pure Chemical Corporation) *n*-Butyllithium, in *n*-hexane, 1.57 mol/L (Kanto Chemical Co., Inc.) Trimethyltin Chloride (Tokyo Chemical Industry Co, Ltd.) Pd₂(dba)₃ (dba = dibenzylideneacetone) (Tokyo Chemical Industry Co, Ltd.) 2-Dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos) (Strem Chemicals, Inc.)

Commercially available solvents:

Acetone (super dehydrated grade, FUJIFILM Wako Pure Chemical Corporation), MeOH (deoxidized grade, FUJIFILM Wako Pure Chemical Corporation), toluene (deoxidized grade, FUJIFILM Wako Pure Chemical Corporation) used without purification.

Tetrahydrofuran (super dehydrated grade, FUJIFILM Wako Pure Chemical Corporation) was purified by

passage through solvent purification columns under N2 pressure.1

Compounds prepared as described in the literatures:

4,4'-Dibromo-2,2'-dihydroxyazobenzene $(1)^2$

13,13'-(2,7-Dibromo-9H-fluoren-9-ylidene)bis[2,5,8,11-tetraoxatridecane] (2)^{3,4}

Synthetic procedures and characterization

Synthesis of TAzPh



In a 50 mL round bottom flask, 1 (0.328 g, 0.88 mmol, 1 equiv.), diphenyltin(IV)oxide (0.382 g, 1.32 mmol, 1.5 equiv.) and 15 mL of acetone were added under N₂. Then, the solution was stirred at 60 °C for 4 h. After the reaction, the mixture was filtered to remove unreacted diphenyltin(IV) oxide, and the solvent was removed with a rotary evaporator to afford **TAzPh** (0.334 g, 0.520 mmol, 59%) as a violet crystal.

¹H NMR (CDCl₃, 400 MHz) δ 7.93–7.73 (m, J_{H_Sn} = 39.9 Hz, 4H), 7.57 (d, J = 8.7 Hz, 1H), 7.44–7.42 (m, 7H), 7.31 (d, J = 2.2 Hz, 1H), 7.29 (d, J = 2.0 Hz, 1H), 7.01 (dd, J = 8.7, 2.1 Hz, 1H), 6.87 (dd, J = 8.8, 2.2 Hz, 1H) ppm. ¹³C{¹H} NMR (CDCl₃, 400 MHz) δ 162.1, 160.9, 138.4, 136.5, 136.3, 136.2 (J_{C-Sn} = 27.1 Hz), 136.2, 132.3, 130.9 (J_{C-Sn} = 9.1 Hz), 129.3, 129.1 (J_{C-Sn} = 43.6 Hz), 126.5, 123.2, 122.6, 121.8, 118.1 ppm. ¹¹⁹Sn NMR (CDCl₃, 149 MHz) δ –364.1 ppm. HRMS (ESI) calcd. for C₂₄H₁₆Br₂N₂O₂Sn [M]⁻: 641.8580; found: 641.8575. Elemental analysis calcd. for C₂₄H₁₆Br₂N₂O₂Sn: C 44.84 H 2.51 N 4.36 Br 24.86, found: C 44.60 H 2.56 N 4.26 Br 24.63.



Chart S1. ¹H NMR spectrum of TAzPh in CDCl₃ at 400 MHz.



Chart S2. ¹³C{¹H} NMR spectrum of TAzPh in CDCl₃ at 100 MHz.



Chart S3. ¹¹⁹Sn NMR spectrum of TAzPh in CDCl₃ at 149 MHz.

Synthesis of TAzMe



In a 100 mL round bottom flask, **1** (0.559 g, 1.50 mmol, 1 equiv.), dimethyltin(IV)dichloride (0.330 g, 1.50 mmol, 1 equiv.), NaOH (0.120 g, 3.00 mmol, 2 equiv.) and 50 mL of MeOH were added under N₂. Then, the solution was stirred at 80 °C for 12 h. Insoluble materials were filtered, and the solution was concentrated in vacuo. The obtained violet solid was purified by recrystallization with THF and hexane to afford **TAzMe** (0.579 g, 1.12 mmol, 74%) as a black crystal.

¹H NMR (CDCl₃, 400 MHz) δ 7.58 (d, J = 8.8 Hz, 1H), 7.41 (m, 1H), 7.02 (d, J = 1.7 Hz, 1H), 6.99-6.96 (m, 2H), 6.86 (dd, J = 2.1, 8.6 Hz, 1H), 0.82 (s, J_{H-Sn} = 38.6 Hz, 6H) ppm. ¹³C {1H} NMR (CDCl₃, 400 MHz) δ 162.0, 160.2, 136.5, 136.2, .135.8, 131.9, 129.2, 126.4, 122.8, 122.4, 121.5, 118.0, 1.8 ppm. ¹¹⁹Sn NMR (CDCl₃, 149 MHz) δ –178.3 ppm. HRMS (ESI) calcd. for C₁₄H₁₂Br₂N₂O₂Sn [M]⁻: 517.8267; found: 517.8266. Elemental analysis calcd. for C₁₄H₁₂Br₂N₂O₂Sn: C 32.41 H 2.33 N 5.40 Br 30.80, found: C 32.32 H 2.38 N 5.49 Br 30.61.



Chart S4. ¹H NMR spectrum of TAzMe in CDCl₃ at 400 MHz.



Chart S5. ¹³C{¹H} NMR spectrum of TAzMe in CDCl₃ at 100 MHz.



Chart S6. ¹¹⁹Sn NMR spectrum of TAzMe in CDCl₃ at 149 MHz.

Synthesis of 3



Compound **2** was prepared according to the previous report.^[2,3] A solution of *n*-BuLi (1.57 M in hexane, 1.37 mL, 2.14 mmol, 2.2 equiv.) was slowly added to a solution of **2** (0.686 g, 0.974 mmol, 1 equiv.) in THF (40 mL) at -78 °C. After 1 h, trimethyltin chloride (0.485 g, 2.44 mmol, 2.5 equiv.) in THF (10 mL) was added at -78 °C and the mixture was stirred for 16 h at room temperature. Saturated aqueous NH₄Cl was added to the reaction mixture, and the organic layer was extracted with EtOAc. The organic layer was washed with brine and dried over MgSO₄. MgSO₄ was removed by filtration, and the solvent was removed with a rotary evaporator. The obtained yellow oil **3** (0.805 g, 0.923 mmol, 95%) was used for the next reaction without further purification.

¹H NMR (CDCl₃, 400 MHz) δ 7.64 (d, J = 7.3 Hz, 2H), 7.49 (s, 2H), 7.44 (d, 2H, J =7.3 Hz), 3.59-3.49 (m, 16H), 3.43-3.39 (m, 4H), 3.35 (s, 6H), 3.24-3.20 (m, 4H), 2.77 (t, J =7.8 Hz, 4H), 2.38 (t, J =7.6 Hz, 4H), 0.33 (m, $J_{\text{H-Sn}}$ = 27.4 Hz, 18H) ppm. ¹³C{¹H} NMR (CDCl₃, 400 MHz) δ 148.1, 141.6, 140.6, 134.5, 130.1, 119.3, 71.9, 70.5, 70.5, 70.4, 70.4, 69.9, 67.2, 59.0, 51.0, 39.5, -9.3 ($J_{\text{C-Sn}}$ = 17.0 Hz) ppm. HRMS (ESI): [M+Na]⁺ Calcd., 897.2381; Found, 897.2405.



Chart S8. ¹³C{¹H} NMR spectrum of 3 in CDCl₃ at 100 MHz.

Synthesis of P-TAzPh



A mixture of **TAzPh** (0.137 g, 0.214 mmol, 1 equiv.), **3** (0.186 g, 0.214 mmol, 1 equiv.), $Pd_2(dba)_3$ (0.0059 g, 0.0064 mmol, 0.03 equiv.), XPhos (0.0061 g, 0.013 mmol, 0.06 equiv.) in toluene (4.0 mL) was stirred at 80 °C for 48 h under N₂ atmosphere. After cooling to room temperature, the solution was poured into a large amount of hexane to collect the polymer by filtration. Additionally, the part of high molecular weight was fractionated by HPLC to afford **P-TAzPh** (0.0381 g, 17%) as a dark blue solid.

 $M_n = 5,300, M_w = 7,100, M_w/M_n = 1.4.$ ¹H NMR (CDCl₃, 400 MHz) δ 8.01 (br), 7.90 (br), 7.79 (br), 7.73 (br), 7.46 (br), 7.15 (br), 3.55 (br), 3.49 (br), 3.42 (br), 3.33 (br), 2.88 (br), 2.53 (br) ppm; ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 136.5, 71.9, 70.5, 70.5, 59.0 ppm. The other ¹³C{¹H} signals were not detected probably because of broadening peaks in a polymer. ¹¹⁹Sn NMR signal was not detected probably because of broadening peaks in a polymer. In place of ¹¹⁹Sn NMR, we confirmed the preservation of tin atom after polymerization by detection of repeating units from a MALDI-TOF MS measurement (negative, matrix: *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB)).



Chart S9. ¹H NMR spectrum of P-TAzPh in CDCl₃ at 400 MHz.



Chart S10. ${}^{13}C{}^{1}H$ NMR spectrum of P-TAzPh in CDCl₃ at 100 MHz.



Chart S11. ¹¹⁹Sn NMR spectrum of P-TAzPh in CDCl₃ at 149 MHz.



Chart S12. MADLI-TOF MS spectrum of P-TAzPh.

Synthesis of P-TAzMe



A mixture of **TAzMe** (0.107 g, 0.205 mmol, 1 equiv.), **3** (0.179 g, 0.205 mmol, 1 equiv.), $Pd_2(dba)_3$ (0.0056 g, 0.0062 mmol, 0.03 equiv.), XPhos (0.0059 g, 0.012 mmol, 0.06 equiv.) in toluene (4.0 mL) was stirred at 80 °C for 48 h under N₂ atmosphere. After cooling to room temperature, the solution was poured into a large amount of hexane to collect the polymer by filtration. Additionally, the part of high molecular weight was fractionated by HPLC to afford **P-TAzMe** (0.0463 g, 25%) as a dark blue solid.

 $M_n = 6,200, M_w = 8,200, M_w/M_n = 1.3.$ ¹H NMR (CDCl₃, 400 MHz) δ 7.92 (br), 7.79 (br), 7.76 (br), 7.72 (br), 7.19 (br), 7.15 (br), 3.57-3.50 (m), 3.40 (br), 3.34 (t), 3.22 (br), 2.85 (br), 2.48 (br), 0.91-0.84 (m) ppm; ¹³C{¹H} NMR (CDCl₃, 100 MHz) δ 126.8, 117.4, 71.9, 70.5, 70.5, 70.5, 70.4, 70.0 (br), 67.1 (br), 59.0, 1.5 ppm. The other ¹³C{¹H} signals were not detected probably because of broadening peaks in a polymer. ¹¹⁹Sn NMR (CDCl₃, 149 MHz) δ –179.9 (br). We also confirmed the preservation of tin atom after polymerization by detection of repeating units from a MALDI-TOF MS measurement (negative, matrix: *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl- 2-propenylidene]malononitrile (DCTB)).



Chart S13. ¹H NMR spectrum of P-TAzMe in CDCl₃ at 400 MHz.



Chart S14. ${}^{13}C{}^{1}H$ NMR spectrum of P-TAzMe in CDCl₃ at 100 MHz.



Chart S15. ¹¹⁹Sn NMR spectrum of P-TAzMe in CDCl₃ at 149 MHz.



Chart S16. MADLI-TOF MS spectrum of P-TAzMe.





Figure S1. (A) UV–vis absorption and (B) PL spectra and (C) photographs under room light (upper) and irradiated by 365 nm (below) of TAzMe, TAzPh, P-TAzMe and P-TAzPh (1.0×10^{-5} M for monomers and 1.0×10^{-5} M per repeating unit for polymers) in toluene and CHCl₃ and toluene/solvents(DMSO, DMF, MeOH, MeCN) = 99/1 v/v.

Titration



Figure S2. Titration spectra of (A) UV–vis absorption and (B) PL of TAzMe in mixed solvents $(1.0 \times 10^{-5} \text{ M})$.



Figure S3. Titration spectra of (A) UV-vis absorption and (B) PL of TAzPh in mixed solvents $(1.0 \times 10^{-5} \text{ M})$.



Figure S4. Titration spectra of (A) UV–vis absorption and (B) PL of **P-TAzMe** in mixed solvents $(1.0 \times 10^{-5} \text{ M per repeating unit})$.



Figure S5. Titration spectra of (A) UV–vis absorption and (B) PL of **P-TAzPh** in mixed solvents $(1.0 \times 10^{-5}$ M per repeating unit).

Summary of absolute PL quantum yields of TAz compounds

Solvent vol%	0	0.5	1	2	5	10	20	30	40	50	60	70	80	90	99
toluene	18.0^{b}	-	_	_	_	_	-	-	-	-	-	_	-	-	_
CHCl ₃	16.5^{b}	_	-	-	-	-	-	-	-	-	-	-	-	-	-
DMSO	-	16.3	15.6	13.9	9.4	4.7	2.0	1.5	1.5	1.6	1.2	1.2	1.2	1.4	1.3
DMF	-	16.7	16.5	16.4	15.1	12.4	8.6	4.4	4.1	3.2	2.8	1.9	1.7	1.7	1.3
MeOH	-	17.4	17.5	17.0	16.1	15.2	13.9	12.5	11.4	9.8	8.7	7.5	6.5	5.6	4.8
MeCN	-	17.2	17.0	16.7	16.5	15.8	14.8	13.7	12.4	11.6	9.1	6.9	5.8	4.7	4.0

Table S1. Absolute PL quantum yields (%) of TAzMe^a

^{*a*} Measured in mixed solutions $(1.0 \times 10^{-5} \text{ M}, \text{ toluene/solvent})$ excited at absorption maxima.

^{*b*} In pure toluene or CHCl₃.

Table S2. Absolut	e PL quantum	yields	(%) oi	f TAzPh ^a
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Solvent															
vol%	0	0.5	1	2	5	10	20	30	40	50	60	70	80	90	99
toluene	15.6 ^a	-	—	-	-	-	_	_	_	—	—	—	—	_	—
CHCl ₃	15.7 ^a	_	-	-	-	-	_	-	-	-	-	-	-	-	-
DMSO	-	15.5	15.3	14.5	12.3	7.8	4.6	3.9	3.8	4.0	3.7	3.7	3.8	3.5	3.7
DMF	-	15.4	15.5	15.1	14.1	12.1	10.0	7.2	5.1	3.7	3.6	3.5	3.7	3.7	4.1
MeOH	-	15.5	15.1	14.8	14.0	13.4	12.2	11.7	10.7	9.8	8.9	8.3	7.4	6.9	6.7
MeCN	-	15.5	15.0	14.8	14.4	13.6	12.3	11.1	9.7	8.7	8.0	7.0	6.4	5.1	4.1

^{*a*} Measured in mixed solutions $(1.0 \times 10^{-5} \text{ M}, \text{ toluene/solvent})$ excited at absorption maxima.

^{*b*} In pure toluene or CHCl₃.



Figure S6. Plots of absolute PL quantum yields (%) versus solvents (vol%) in toluene $(1.0 \times 10^{-5} \text{ M per repeating unit})$ from Tables S1 and S2.

Solvent	0	0.5	1	2	5	10	20	30	40	50	60	70	80	90	99
vol%															
toluene	24.4^{b}	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CHCl ₃	31.2^{b}	-	_	_	_	_	-	-	-	-	-	-	-	-	-
DMSO	-	27.0	26.8	26.5	22.0	10.0	2.4	1.2	1.1	0.9	1.1	1.1	1.0	0.9	1.0
DMF	-	27.0	26.5	26.3	24.5	22.5	12.7	2.3	1.2	1.3	1.8	2.0	2.4	2.5	2.6
MeOH	-	25.7	26.1	26.6	27.3	25.9	23.1	19.7	16.6	13.1	10.8	7.5	4.5	2.9	2.0
MeCN	-	28.2	26.9	29.0	27.7	25.2	25.1	20.8	16.0	12.1	8.8	5.0	2.5	1.1	0.7

Table S3. Absolute PL quantum yields (%) of P-TAzMe^a

^{*a*} Measured in mixed solutions $(1.0 \times 10^{-5} \text{ M per repeating unit, toluene/solvent})$ excited at absorption maxima.

^{*b*} In pure toluene or CHCl₃.

Table S4. Absolute PL quantum yields (%) of P-TAzPh^a

Solvent vol%	0	0.5	1	2	5	10	20	30	40	50	60	70	80	90	99
toluene	19.2 ^{<i>a</i>}	-	-	-	-	-	-	-	-	-	-	-	-	-	-
CHCl ₃	16.7 ^a	_	-	-	-	-	-	-	-	-	-	-	-	-	-
DMSO	-	18.8	17.5	16.6	14.3	10.2	3.6	2.0	2.5	2.4	2.6	2.4	2.9	2.1	2.2
DMF	-	17.4	16.8	15.9	14.9	13.1	6.0	1.8	2.3	3.7	4.8	5.0	5.0	4.9	5.1
MeOH	-	18.3	19.0	19.2	18.0	16.5	15.1	13.1	11.8	10.1	8.0	6.2	4.2	2.5	1.6
MeCN	-	18.6	18.2	18.2	17.8	15.8	13.5	10.2	7.1	4.1	2.5	1.5	1.4	1.3	1.2

^a Measured in mixed solutions (1.0×10⁻⁵ M per repeating unit, toluene/solvent) excited at absorption

maxima.

^{*b*} In pure toluene or CHCl₃.



Figure S7. Plots of absolute PL quantum yields (%) versus solvents (vol%) in toluene $(1.0 \times 10^{-5} \text{ M per repeating unit})$ from Tables S3 and S4.

Determination of binding constant

Determination of binding constants for the TAz complexes was carried out by means of an absorption titration technique in toluene at room temperature (25 °C) (Figure S8) according to our previous research.⁵ We assumed equilibrium 1:1 binding of a TAz complex and a solvent (Scheme S1). The concentration of a TAz complex, $[H]_0$ was kept constant and the concentration of guest (DMSO or DMF), [G], was varied in non-coordinating solvent, toluene. The mixed solutions of a TAz complex and guest from toluene/guest = 100/0 to 1/99 v/v were prepared, and UV–vis absorption spectra were recorded. The host-guest complexation immediately reach equilibrium after preparation of the mixed solutions. The binding constants were determined by a non-linear curve fitting analysis of hypsochromic shifts and reduction of absorption spectra by increasing guest concentration from toluene/solvent = 100/0 to 9/1 v/v solutions because the raising solvent polarity affected the shape of absorption spectra over toluene/solvent = 9/1 v/v solution components. The *y*-axis is ΔA and the *x*-axis is [G]. The binding constants $K_{a,guest}$ were calculated from eq(1) using non-linear curve fitting (A: absorbance, b: optical path length, ε : molar extinction coefficient, $\Delta \varepsilon = \varepsilon(100/0) - \varepsilon(1/99)$). A(x/y) or $\varepsilon(x/y)$ means a value of an absorbance or a molar extinction coefficient of a sample in toluene/solvent = x/y v/v, respectively.

$$\Delta A = (b\Delta \varepsilon/2K_{guest})[1 + K_{a,guest}[G] + K_{guest}[H_0] - \{(1 + K_{guest}[H_0] + K_{guest}[G])^2 - 4K_{guest}^2[G][H_0]\}^{1/2}]$$
(1)



Scheme S1. Equilibrium reaction between host TAz complexes (R = Me, Ph) and guest solvents (DMSO, DMF).

TAzMe in DMSO



toluene/DMSC v/v	[DMSO] / M	∆Aª					
100/0	0	0					
99.5/0.5	0.070	0.0136					
99/1	0.14	0.0201					
98/2	0.28	0.0314					
95/5	0.70	0.0429					
9/1	1.4	0.0536					
^a ΔA = A(100/0) − A, at 600 nm							



toluene/DMF v/v	[DMF] / M	∆Aª					
100/0	0	0					
99.5/0.5	0.065	0.0033					
99/1	0.13	0.0049					
98/2	0.26	0.0091					
95/5	0.65	0.0175					
9/1	1.3	0.0307					
^a ΔA = A(100/0) − A, at 600 nm							



0.5

ΔA

0.02

0;

0

toluene/DMSO v/v	[DMSO] / M	ΔAª
100/0	0	0
99.5/0.5	0.070	0.0312
99/1	0.14	0.0435
98/2	0.28	0.0551
95/5	0.70	0.0662
9/1	1.4	0.0707

^a ∆A = A(100/0) – A, at 600 nm



4

1.5

K_{DMSO} = 11 M⁻¹

 $\begin{array}{l} b = 1 \ {\rm cm} \\ \Delta \varepsilon = 7,270 \ {\rm M}^{-1} {\rm cm}^{-1} \\ [H]_0 = 1.0 \times 10^{-5} \ {\rm M} \end{array}$

[DMSO] / M

1.0

Figure S8. Absorption titration and non-linear curve fitting graph and parameters of **TAzMe** and **TAzPh** with DMSO and DMF in toluene at room temperature.

Vapochromism of film



Figure S9. Schematic illustration of vapor diffusion method (30 min) and dry process (30 min) to investigate vapochromism in film.

UV-vis absorption spectra in film



Figure S10. UV–vis absorption spectra of (A) **P-TAzMe** and (B) **P-TAzPh** in film before and after solvent annealing for 30 min, and recovery test by drying the film for 30 min at ambient condition.

PL spectra in film



Figure S11. PL spectra of (A) **P-TAzMe** and (B) **P-TAzPh** in film before and after solvent annealing for 30 min, and recovery test by drying the film for 30 min at ambient condition.

Computational details for theoretical calculation

The Gaussian 16 program package⁶ was used for computation. We optimized the structures of the **TAzMe, TAzPh, M-TAzMe** and **M-TAzPh**, and their DMSO adducts **TAzMe-DMSO**, **TAzPh-DMSO**, **M-TAzMe-DMSO** and **M-TAzPh-DMSO** in the ground S₀ states and calculated their molecular orbitals. The DFT was applied for the optimization of the structures in the S₀ states at B3LYP/6-311G(d,p) level for C, H, N, O, Br, S and LanL2DZ for Sn. We calculated the energy of the S₀–S₁ transitions with optimized geometries in the S₀ states by time-dependent (TD) DFT at B3LYP/6-311G(d,p) level for C, H, N, O, Br, S and LanL2DZ for Sn.

Chemical structures





Figure S12. (A) Calculated HOMO and LUMO energy levels, and (B) calculated $S_0 \rightarrow S_1$ transition bands and oscillator strengths (*f*) with DFT and TD-DFT.



Figure S13. Side view of optimized structures, and selected Kohn–Sham orbitals (isovalue = 0.02) of **TAzMe, TAzMe-DMSO, TAzPh and TAzPh-DMSO**.



Figure S14. Side view of optimized structures, and selected Kohn–Sham orbitals (isovalue = 0.02) of **M**-TAZMe, M-TAZMe-DMSO, M-TAZPh and M-TAZPh-DMSO.



Figure S15. (A) The optimized structures and simulated Sn–O (DMSO) bond lengths of **TAzPh-DMSO** and **M-TAzPh-DMSO** with DFT. (B) The relationship between simulated Sn–O (DMSO) bond lengths of TAz-DMSO compounds and measured binding constants (K_{DMSO}) in toluene at ambient temperature from ref. 5.

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