Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

for

A New BODIPY-Derived Ratiometric Senor of Internal Charge Transfer (ICT) Effect：Colorimetric/Fluorometric Sensing for Ag^+

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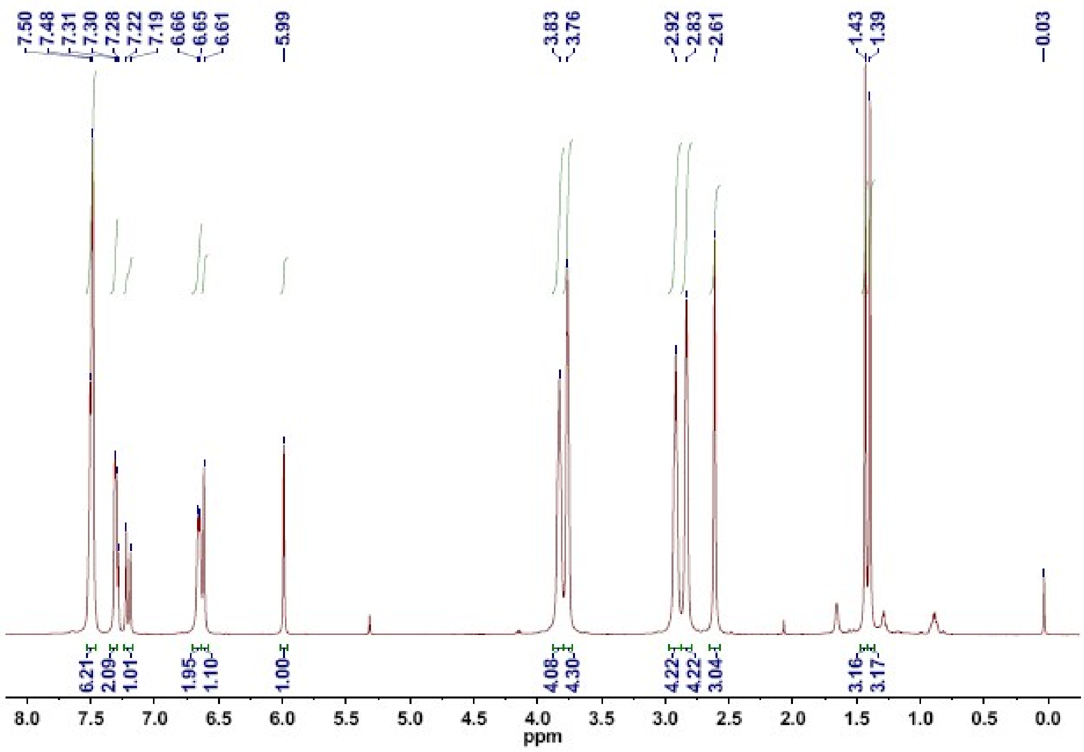

Fig. S1 ^{1}H-NMR spectrum of **BDP-ODTAC** in $CDCl_3$.

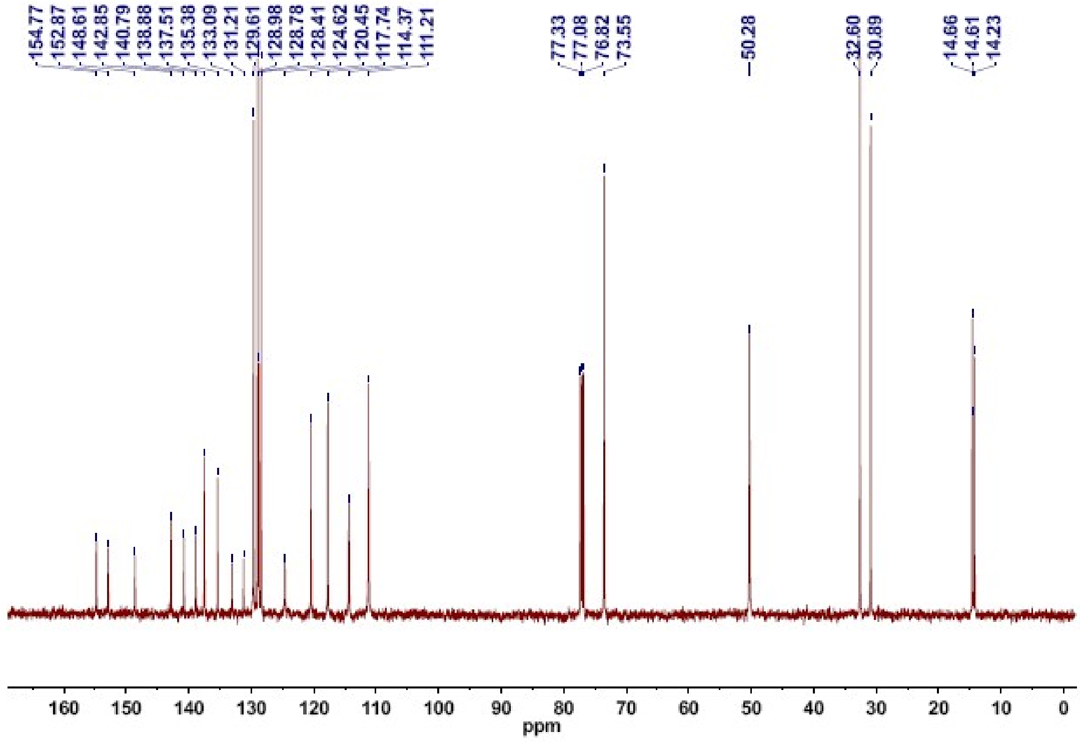

Fig. S2 ^{13}C-NMR spectrum of **BDP-ODTAC** in $CDCl_3$.

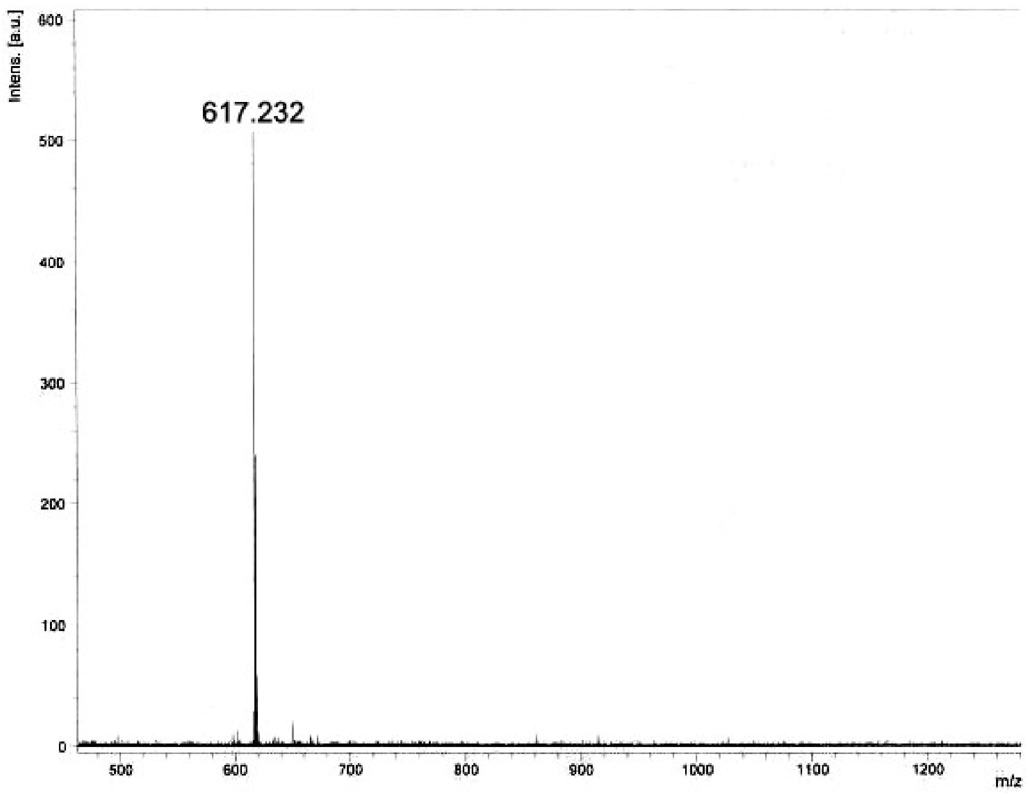

Fig. S3 ESI-MS spectrum of **BDP-ODTAC**.

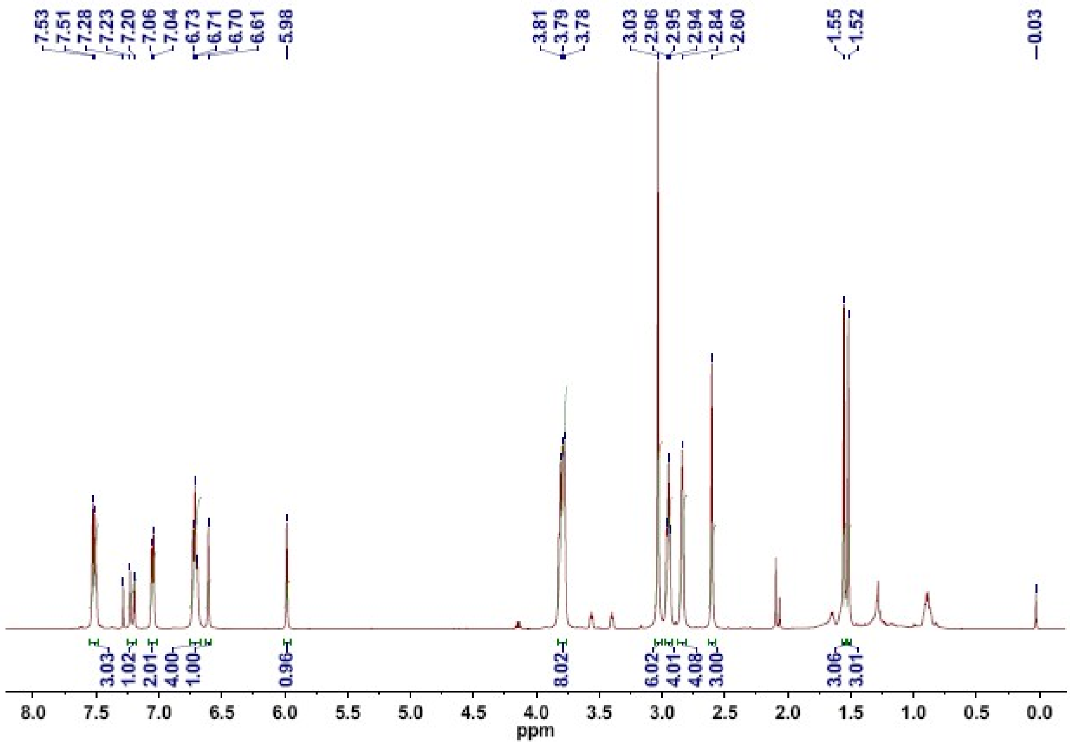

Fig. S4 ^{1}H-NMR spectrum of **ODTAC-BDP** in $CDCl_3$.

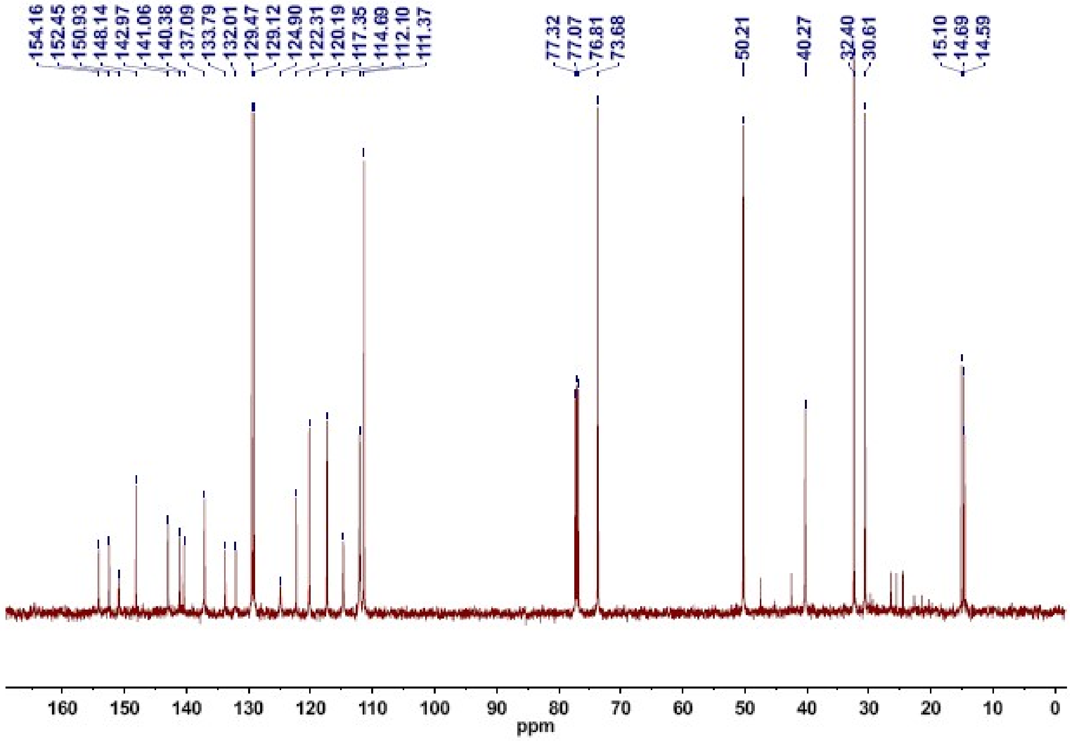

Fig. S5 ^{13}C-NMR spectrum of **ODTAC-BDP** in $CDCl_3$.

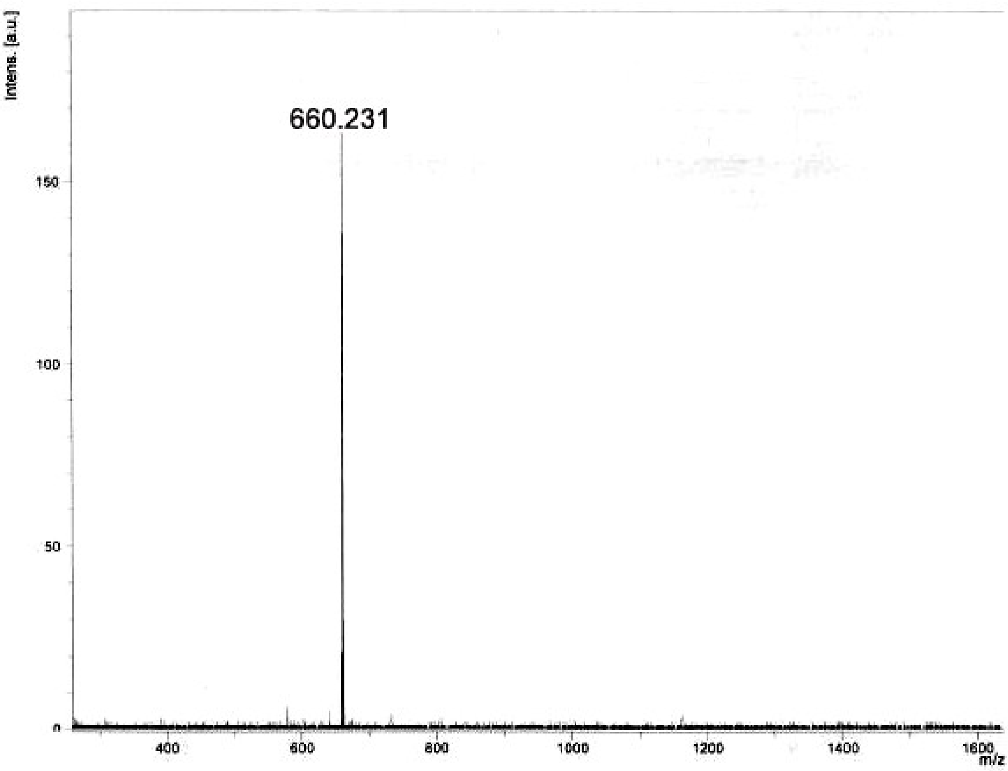

Fig. S6 ESI-MS spectrum of **ODTAC-BDP**.

S1. Determination of quantum yields

Fluorescence quantum yield of **BDP-ODTAC**, **ODTAC-BDP** and Ag^+/**BDP-ODTAC**, Ag^+/**ODTAC-BDP** complex were determined in MeOH by using Rhodamine B solution (Φ_f = 0.4, MeOH) as references. The quantum yields were calculated using Eq.1:

$$\Phi_u = [(A_s F_u n^2) / (A_u F_s n_0^2)]\ \Phi_s \qquad \text{(Eq.1)}$$

Where A_s and A_u are the absorbance of the reference and sample solution at the reference excitation wavelength, F_s and F_u are the corresponding integrated fluorescence, n and n_0 are the refractive indexes of the solvents for the sample and reference solutions. Absorbance of samples and references at their respective excitation wavelengths was controlled to be lower than 0.05.

S2. Dissociation constant determination for Ag^+/BDP-ODTAC complex

Fluorescence measurement was carried out with the series of solution which the ratio of $[Ag^+]$/[**BDP-ODTAC**] were 0~500. The dissociation constant of Ag^+/**BDP-ODTAC** complex were calculated using Eq.2:

$$[Ag^+] = K_d\,(R-R_f)\,S_{f2} / (R_b-R)S_{b2} \qquad \text{(Eq.2)}$$

Where R is the ratio of the dye's fluorescence intensities F_1 and F_2 at just two excitation wavelengths λ_1 and λ_2, S_{f2}/S_{b2} is the ratio $F_{2free}/F_{2banding}$ at the excitation wavelength λ_2.

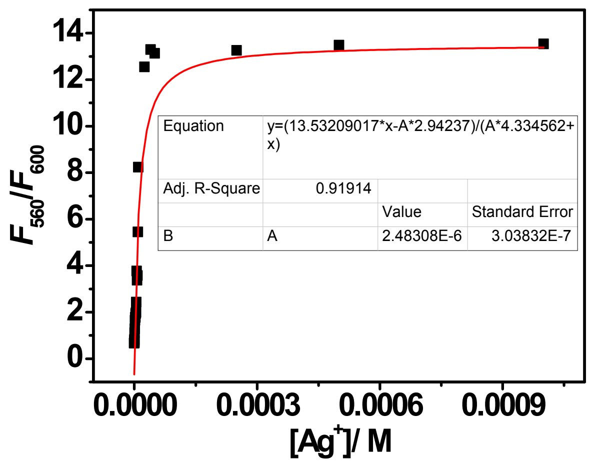

Fig. S7 Ratio of emission at 675 nm upon excitation at 560 nm to that upon excitation at 600 nm, F_{560}/F_{600}, of **BDP-ODTAC** (5 μM) as a function of $[Ag^+]$ in MeOH.

S3. Dual excitation ratiometric sensing reversibility of BDP-ODTAC for Ag^+

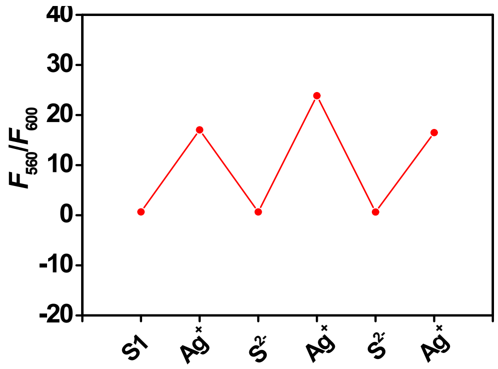

Fig. S8 Ratio of emission at 675 nm upon excitation at 560 nm to that upon excitation at 600 nm, F_{560}/F_{600}, of **BDP-ODTAC** (5 μM) induced by adding Ag^+ (12 mM) and S^{2-} (12 mM) in sequence. λ_{em}, 675 nm. S1, **BDP-ODTAC**.

S4. Fluorescent sensing selectivity of BDP-ODTAC in methanol

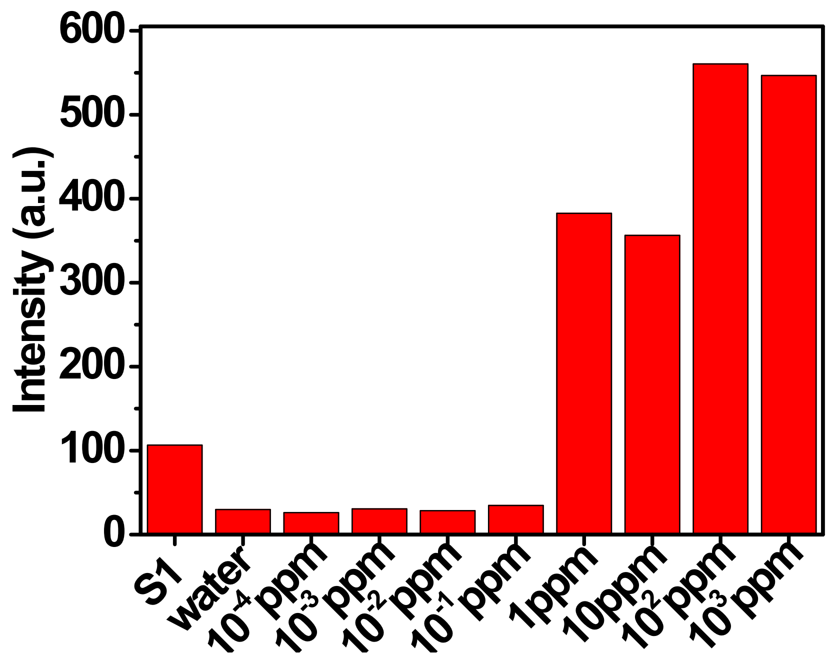

Fig. S9 Emission intensity of **BDP-ODTAC** (5 μM) at 587 nm determined in methanol upon adding Ag^+ aqueous to the marked Ag^+ concentration. Water content in final solution is lower than 4% in volume. λ_{ex}, 560 nm.

S5. Fluorescent sensing behaviors of ODTAC-BDP in methanol

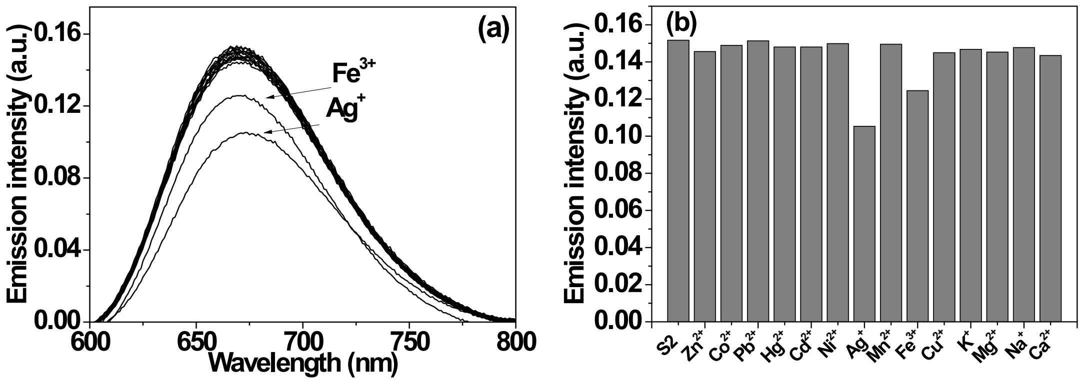

Fig. S10 (a) Emission spectra of **ODTAC-BDP** (5 μM) in CH_3OH determined upon adding different metal cations, and (b) the related emission intensity at 675 nm. λ_{ex}, 591 nm. The final concentration for Fe^{3+}, Hg^{2+}, Zn^{2+}, Cd^{2+}, Ni^{2+}, Mn^{2+}, Co^{2+}, Cu^{2+}, Ag^{+}, and Pb^{2+} is 10 μM, for K^{+}, Ca^{2+}, Na^{+}, and Mg^{2+} is 1 mM. S2: sensor **ODTAC-BDP**

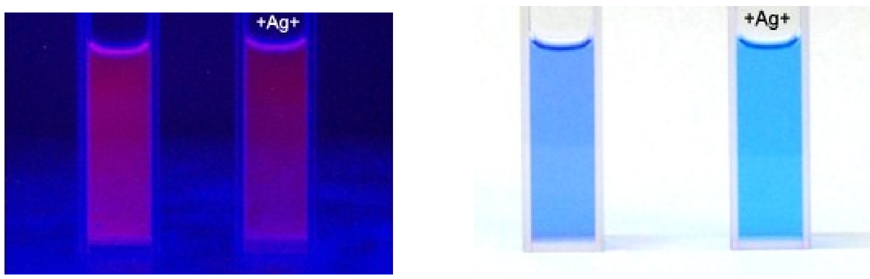

Fig. S11 (Left) Photograph of **ODTAC-BDP** (5 μM) in methanol before and after Ag^{+} addition (2 equiv) upon irradiation with an UV lamp of 365 nm. (Right) Photograph of **ODTAC-BDP** (5 μM) in methanol before and after Ag^{+} addition (2 equiv) in ambient condition.