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Distinguishing Förster Resonance Energy Transfer and Solvent-Mediated Charge-Transfer Relaxation Dynamics in a Zinc(II) Indicator: A Femtosecond Time-Resolved Transient Absorption Spectroscopic Study

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Supporting Information

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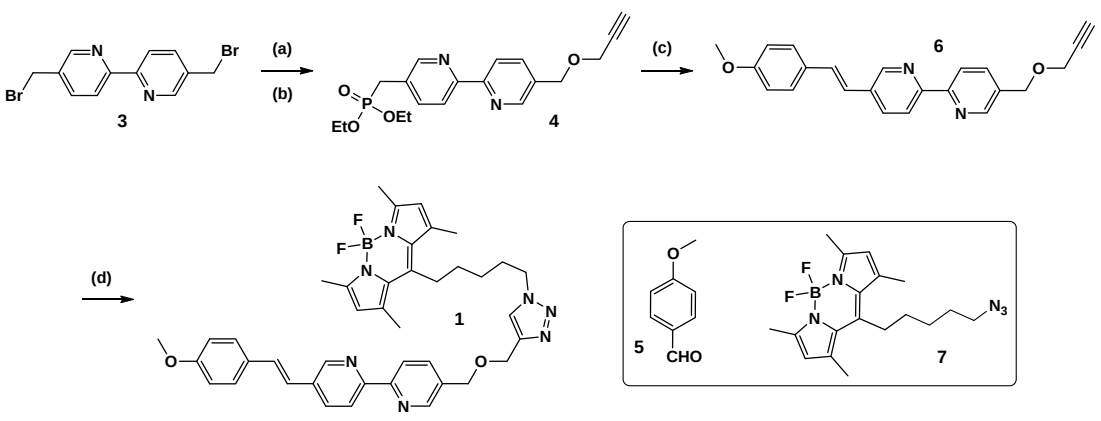
Materials and general methods

Reagents and solvents were purchased from various commercial sources and used without further purification unless otherwise stated. All reactions were carried out in oven- or flame-dried glassware. Analytical thin-layer chromatography (TLC) was performed using pre-coated TLC plates with silica gel 60 F254 or with aluminum oxide 60 F254 neutral. Flash column chromatography was performed using 40-63 μm (230-400 mesh ASTM) silica gel or alumina (80-200 mesh, pH 9-10) as the stationary phases. Silica and alumina gel was flame-dried under vacuum to remove adsorbed moisture before use. ^{1}H and ^{13}C NMR spectra were recorded at 300 MHz and 125 MHz (on two different instruments), respectively. All chemical shifts were reported in δ units relative to tetramethylsilane.

Synthesis and characterization

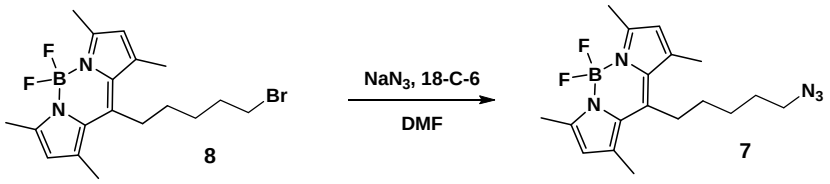


Scheme S1. Reagents and conditions: (a) NaH, propargyl alcohol, THF, 0 °C to rt; (b) $(EtO)_3P$, 110 °C, 2 h, 31% for two steps; (c) compound **5**, KHDMS, -78 °C to rt, 53%; (d) compound **7**, $Cu(OAc)_2 \cdot H_2O$, sodium ascorbate, TBTA (cat.), 12 h, 62%.

Compound 4. NaH (108 mg, 60% dispersion in mineral oil, 2.71 mmol) was suspended in dry THF (5.0 mL) in a flame-dried flask. The reaction mixture was cooled to 0 °C. Propargyl alcohol (160 μL, 2.74 mmol) was added slowly and stirred under an argon atmosphere for 10 min. The solution was slowly added to 5,5'-bis(bromomethyl)-2,2'-dipyridyl[S1] (**3**, 923 mg, 2.7 mmol) in THF (40 mL) and stirred for 2 h. Subsequently, most of the THF was removed under vacuum. The residue was partitioned between

CH_2Cl_2 and a saturated brine solution. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was heated at 110 °C in $(EtO)_3P$ (4.0 mL). After 2 h, excess $(EtO)_3P$ was removed under reduced pressure. The residue was purified using silica chromatography, eluted by CH_3OH in ethyl acetate (gradient 0-5%). The yield was 310 mg (31%). ^{1}H NMR (300 MHz, $CDCl_3$) δ/ppm 8.65 (d, *J* = 1.2 Hz, 1H), 8.57 (s, 1H), 8.38-8.34 (m, 2H), 7.85-7.78 (m, 2H), 4.69 (s, 2H), 4.22 (d, *J* = 2.4 Hz, 2H), 4.11-4.01 (m, 4H), 3.19 (d, *J* = 21.6 Hz, 2H), 2.51 (t, *J* = 2.4 Hz, 1H), 1.26 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ/ppm 155.6, 154.6, 150.1, 148.9, 138.2, 136.9, 132.9, 128.2, 120.9, 79.2, 75.3, 68.8, 62.5, 57.5, 31.6, 30.5, 16.5. HRMS (ESI+) (*m/z*): $[M+H]^+$ calcd for $C_{19}H_{24}N_2O_4P$ 375.1473, found 375.1473.

Compound 6. In a flame-dried flask compound **4** (100 mg, 0.27 mmol) and 4-methoxy-benzaldehyde (**5**, 43 mg, 0.32mmol) were dissolved in dry THF (20 mL) and cooled to -78 °C. Potassium hexamethyldisilazide (640 μL, 0.5 M in toluene, 0.32 mmol) was added dropwise. Upon completing the addition, the stirring was continued for 3 h while the temperature rose to rt. The reaction mixture was then diluted with ethyl acetate (50 mL) and filtered through a short pad of silica gel and washed with ethyl acetate. The solvent was removed under reduced pressure. The crude product was purified by column chromatography using ethyl acetate in CH_2Cl_2 (gradient 0-10%). The yield was 51 mg (53%). ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm 8.74 (s, 1H), 8.66 (s, 1H), 8.39 (t, *J* = 6.9 Hz, 2H), 7.95 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.83 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 16.8 Hz, 1H), 6.99 (d, *J* = 16.2 Hz, 1H), 6.92 (d, *J* = 9.0 Hz, 2H), 4.69 (s, 2H), 4.24 (d, *J* = 1.8 Hz, 2H), 3.84 (s, 3H), 2.51 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ/ppm 159.9, 155.8, 154.4, 149.1, 148.1, 136.9, 133.6, 133.2, 132.8, 130.7, 129.7, 128.2, 122.6, 121.1, 120.9, 114.9, 79.4, 75.4, 69.0, 57.6, 55.5. HRMS (ESI+) (*m/z*): $[M+H]^+$ calcd for $C_{23}H_{21}N_2O_2$ 357.1603, found 357.1621.



Scheme S2. Synthesis of compound **7**. 18-C-6: 18-crown-6.

Compound 7. Compound **8**[S2] (100 mg, 0.25 mmol), sodium azide (32 mg, 0.5 mmol), and 18-crown-6 (catalytic amount) were stirred in DMF (5 mL) at 50 °C for 12 h. After cooling to rt, the reaction mixture was diluted with ethyl acetate (50 mL), and washed with a saturated NH_4Cl solution (50 mL × 3). The organic layer was separated and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The crude product was purified by column chromatography using CH_2Cl_2 as eluent. The yield was 70 mg (78%). ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm 6.05 (s, 2H), 3.31 (t, *J* = 6.0 Hz, 2H), 2.95 (t, *J* = 7.2 Hz, 2H), 2.51 (s, 6H), 2.41 (s, 6H), 1.72-1.55 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ/ppm 154.1, 146.1, 140.4, 131.6, 121.9, 51.4, 31.5, 28.8, 28.4, 27.5, 16.6, 14.6. HRMS (ESI+) (*m/z*): $[M+Na]^+$ calcd for $C_{18}H_{24}BF_2N_5Na$ 382.1991, found 382.2000.

Compound 1.Compound **6** (17 mg, 0.05 mmol) and azide **7** (17 mg, 0.05 mmol) were dissolved in a CH_2Cl_2-CH_3OH (1:1) mixture (6 mL). Aqueous solutions of sodium ascorbate (0.5 M, 50 μL) and $Cu(OAc)_2 \cdot H_2O$ (0.1 M, 50 μL) were mixed to produce an orange suspension containing the copper(I) catalytic species, which was subsequently added to the stirring solution. TBTA (catalytic amount) was added, and the mixture was stirred for 12 h at rt. It was then partitioned between CH_2Cl_2 and a basic EDTA (0.1 M, pH = 10) solution. The organic fraction was washed with a basic saturated brine solution (pH > 10) for two more times before dried over K_2CO_3. The solvent was removed, and compound **1** was isolated by silica chromatography. Unreacted starting materials were recovered using ethyl acetate in CH_2Cl_2 (0-50%). The column was then eluted with CH_3OH in CH_2Cl_2 (gradient 0-2%) to afford the product. The yield was 21 mg (62%). ^{1}H NMR (300 MHz, $CDCl_3$): δ/ppm 8.73 (s, 1H), 8.64 (s, 1H), 8.37 (t, *J* = 8.4 Hz, 2H), 7.95 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.82 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.53 (s, 1H), 7.49 (d, *J* = 9.0 Hz, 2H), 7.19 (d, *J* = 16.2 Hz, 1H), 6.99 (d, *J* = 16.2 Hz, 1H), 6.92 (d, *J* = 9.0 Hz, 2H), 6.04 (s, 2H), 4.74 (s, 2H), 4.69 (s, 2H), 4.37 (t, *J* = 7.2 Hz, 2H), 3.84 (s, 3H), 2.91 (t, *J* = 7.8 Hz, 2H), 2.49 (s, 6H), 2.37 (s, 6H), 2.00-1.94 (m, 2H), 1.70-1.50 (m, 4H). ^{13}C NMR (125 MHz, $CDCl_3$): δ/ppm 159.9, 155.8, 154.4, 154.2, 148.9, 148.1, 145.8, 145.2, 140.4, 136.8, 133.6, 133.4, 133.3, 131.5, 130.7, 129.7, 128.2, 122.6, 121.9, 121.1, 120.8, 114.4, 70.1, 64.2, 55.5, 50.2, 31.4, 30.3, 28.2, 27.2, 16.6, 14,7. HRMS (ESI+) (*m/z*): $[M+H]^+$ calcd for $C_{41}H_{45}BF_2N_7O_2$ 716.3696, found 716.3713.

General procedure for steady state absorption, emission spectroscopy and fluorescence lifetime measurements

Spectrophotometric and fluorometric titrations were conducted on a Varian Cary 100 Bio UV-Visible Spectrophotometer and a Varian Cary Eclipse Fluorescence Spectrophotometer, respectively, with a 1-cm semi-micro quartz cell (Starna). Fluorescence quantum yields were determined by comparison of the integrated area of corrected emission spectra with that of quinine bisulphate (ϕ_f = 0.54 in 1 N H_2SO_4).[S3-5] Fluorescence lifetimes were determined using a Horiba-Yvon fluorometer nanosecond single-photon counting system employing 370- and 460-nm nanoLED excitation source. Photon count was set at 10,000, the TAC range was 100 ns, the coaxial delay and sync delay were 94 ns and 50 ns, respectively. The fluorescence lifetime values were determined by deconvoluting the instrument response function with exponential decay using DAS6 decay analysis software. The quality of the fit was judged by χ^2 value (< 1.2) and the visual inspection of the residuals.

Table S1. Fluorescence lifetimes of **1**, [Zn(**1**)]$(ClO_4)_2$, [Zn(**2**)]$(ClO_4)_2$, and **3**, excitation sources, collection wavelengths, χ^2 values.

Compound	$\lambda_{(excited)}$, nm	$\lambda_{(collected)}$, nm	τ, ns	χ^2
1	**460**	**510**	**5.74**	**1.10**
3	**460**	**510**	**6.13**	**0.99**
[Zn(2)]$(ClO_4)_2$	**370**	**510**	**3.21**	**0.96**
[Zn(1)]$(ClO_4)_2$	**370**	**510**	**4.01**	**1.13**
[Zn(1)]$(ClO_4)_2$	**460**	**510**	**4.07**	**1.11**

Femtosecond time-resolved transient absorption spectroscopy

Femtosecond time-resolved pump–probe transient absorption experiments were performed using a 1-kHz regeneratively amplified Ti: Sapphire laser system that delivered 800-μJ pulse energies centered at 800 nm. The amplified pulse was characterized by frequency-resolved optical gating (FROG) pulse diagnostics.[S6] The amplified laser output was frequency doubled to generate 400-nm light (200 μJ/pulse), which was attenuated to 400 nJ/pulse and used as the excitation pump pulse. A small portion

(4%) of the fundamental laser output was passed through a sapphire plate to generate the continuum probe pulse that typically extended from 450 nm to 850 nm. The pump–probe time delay was controlled using a retroreflecting mirror mounted on a motorized linear translation stage (Newport), providing 3.3 fs precision. Both pulses were spatially overlapped in the sample-laser interaction region. Differential absorption of the probe was measured as a function of the time delay between the pump and probe by mechanically chopping the pump pulse at 500 Hz. The probe was spectrally dispersed on a silicon diode array to generate a wavelength-resolved differential absorption spectrum that spanned from 450 nm to 800 nm. Data were acquired for two seconds at each pump–probe delay. The instrument response time (120 fs) was determined from the non-resonant response of the pump and probe pulses in toluene. The full dynamic range of the measurements extended from 10 ps before to 3.2 ns after time zero.

Data analysis method: Femtosecond transient absorption

Data fitting used in this work was similar to previously published methods.[S7] Here, temporal integration of data at select wavelengths measured in the transient absorption spectrum provided electronic relaxation kinetic traces. The transient data were fit using an in-house program that uses an iterative least-squares approach. The transient kinetics were fit globally to the sum of multiple exponential decay (or growth) functions:

$$S(t) = g(t) \sum_{i=1}^{n} c_i \cdot e^{-(\frac{t}{\tau_i})} \qquad \text{(S1)}$$

where g(t) is a Gaussian function which deconvoluted the instrument response function (IRF) to the Gaussian pump and probe laser pulses, n was the total number of components, c_i was the amplitude coefficient of the i^{th} component, t was the pump-probe time delay beyond the experimental zero, and τ_i is the relaxation time of the i^{th} component.

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