Electronic Structure and Photophysics of a Supermolecular Iron Complex having a Long MLCT State Lifetime and Panchromatic Absorption

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1. Materials and Synthesis

Synthetic Materials

Tetrahydrofuran (THF) was purchased from Sigma-Aldrich (Inhibitor free, HPLC grade) and distilled over sodium and benzophenone before use. Diisopropylamine was purchased from Sigma-Aldrich (redistilled, 99.95%). All other solvents utilized in syntheses were purchased from Fisher Scientific (HPLC grade). Acetonitrile was dried over calcium hydride and distilled. All other reagents were used as received (Aldrich or Fisher). Chromatographic purification (silica gel 60, 230-400 mesh, EM Science; aluminum oxide, 50-200 µm, 60 Å, Acros Organics; Bio-Beads S-X1, 200-400 mesh, BioRad) of all newly synthesized compounds was accomplished on the bench top.

Synthesis

FePZn and FeNHCPZn were synthesized with PF$_6^-$ counterions. The synthetic route is detailed in Figure S1. Syntheses of 1, 2, 6, and 7 were adapted from established synthetic procedures.

[5-(4-Ethynyl-2,6-dibromopyridyl)-10,20-bis(2,6-bis(3,3-dimethyl-1-butyloxy)phenyl)porphinato]zinc(II) (3). A 100 mL Schlenk flask equipped with a stirbar was charged with 1 (138 mg, 0.38 mmol), 2 (180 mg, 0.19 mmol), Pd$_2$(dba)$_3$ (34.8 mg, 0.038 mmol) and AsPh$_3$ (58.2 mg, 0.19 mmol) under Ar. 40 ml THF and 4 ml diisopropylamine were mixed together and added after being degassed by three freeze-pump-thaw cycles. The mixture was cooled at 0 °C for 1 h and then warmed to RT. When the reaction was complete, the solvent was removed. The compound was then purified by silica gel chromatography (DCM: hexane = 3: 2) to give a green solid (150 mg, 67%, based on 2). $^1$H NMR (400 MHz, acetone-d$_6$, ppm): $\delta$ 10.16 (s, 1H), 9.71 (s, 2H), 9.29 (d, 2H, J = 4 Hz), 8.92 (d, 2H, J = 4 Hz), 8,84 (d, 2H, J = 4 Hz), 8.26 (s, 2H), 7.79 (t, 2H, J = 8 Hz), 7.19 (d, 4H, J = 8 Hz), 3.99 (t, 8H, J = 4 Hz), 0.88 (t, 8H, J = 4 Hz), 0.24 (m, 36H). C$_{63}$H$_{69}$Br$_2$N$_5$O$_4$Zn: m/z = 1183.30, MALDI-TOF: m/z = 1184.68 [M+H]$^+$.

[5-(4-Ethynyl-2,6-bis(1H-imidazol-1-yl)pyridyl)-10,20-bis(2,6-bis(3,3-dimethyl-1-butyloxy)phenyl)porphinato]zinc(II) (4). A mixture of 3 (25 mg, 0.021 mmol), imidazole (4.3 mg, 0.063 mmol), CuI (1.6 mg, 0.008 mmol) and Cs$_2$CO$_3$ (27 mg, 0.084 mmol) were heated in 10 ml dry DMF at 110 °C for two days. After the solvent was removed, the crude product was purified by neutral aluminum oxide chromatography with 5% methanol in DCM as eluent to give a green solid (11 mg, 45%). $^1$H NMR (400 MHz, THF-d$_8$, ppm): $\delta$ 10.01 (s, 1H), 9.69 (d, 2H, J = 4 Hz), 9.16 (d, 2H, J = 4 Hz), 8.91 (d, 2H, J = 4 Hz), 8.33 (m, 2H), 7.95 (m, 2H), 7.73 (m, 2H), 7.12 (d, 4H, J = 8 Hz), 6.88 (m, 2H), 3.96 (t, 8H, J = 8 Hz), 0.76 (t, 8H, J = 8 Hz), 0.4 (m, 36H). C$_{69}$H$_{75}$N$_9$O$_4$Zn: m/z = 1157.52, MALDI-TOF: m/z = 1159.86 [M+1]$^+$.

[5-(4-Ethynyl-2,6-bis(3-methylimidazolium-1-yl)pyridyl)-10,20-bis(2,6-bis(3,3-dimethyl-1-butyloxy)phenyl)porphinato]zinc(II) bis(hexafluorophosphate) (5). A 100 mL round bottom flask equipped with a stirbar was charged with 4 (60 mg, 0.052 mmol) and Me$_3$OBF$_4$ (16.9 mg, 0.114 mmol) under Ar; 40 ml dry DCM was then added. The mixture was stirred at RT for 2 - 3 h. A few drops of water were added to quench the reaction, and the solvent was removed. A small amount of acetonitrile was added to dissolve the mixture. Saturated KPF$_6$ (aqueous solution) was added to precipitate the product. The crude product was filtered and dried. The
compound was then purified by silica gel chromatography (MeCN: H2O: saturated KNO3 (aq) = 90: 9: 1). The green band was collected and evaporated to a 5 ml volume, and saturated KPF6 (aqueous solution) was added to precipitate the product, which was then filtered and dried to give a green solid (30 mg, 39%, based on 4). This material was utilized directly in the following synthetic procedure. C63H69Br2N5O4Zn: m/z=1187.57, MALDI-TOF: m/z =1188.91 [M+H]+.

FeNHCPZn. A 100 mL round bottom flask equipped with a stirbar was charged with 5 (30 mg, 0.02 mmol) and 6 (10.73 mg, 0.02 mmol) under Ar, then 40 ml dry THF was added. The mixture was cooled to −78 °C, then t-BuOK (9.99 mg, 0.088 mmol) dissolved in THF was added. After stirring at −78 °C for 20 min, anhydrous FeBr2 (3.9mg, 0.018 mmol) suspended in THF was added, followed by warming of the reaction to RT. After 1 h, a small amount of water was added and the solution was concentrated. Saturated KPF6 aqueous solution was then added to precipitate the product. The crude product was filtered and dried. The compound was then purified by silica gel chromatography (MeCN: H2O: saturated KNO3 (aq) = 95: 4: 1). The brown band was collected and evaporated to 5 ml, and saturated KPF6 aqueous solution was added to precipitate the product. The crude product was filtered and dried. The compound was then purified by silica gel chromatography (MeCN: H2O: saturated KNO3 (aq) = 95: 4: 1). The brown solid (7 mg, 20%). 1H NMR (400 MHz, CD3CN, ppm): δ 10.12 (s, 1H), 9.85 (d, 2H, J = 4 Hz), 9.26 (d, 2H, J = 4 Hz), 8.95 (d, 2H, J = 4 Hz), 8.79 (d, 2H, J = 4 Hz), 8.39 (s, 2H), 8.22 (d, 2H, J = 2 Hz), 8.21 (t, 1H, J = 8 Hz), 8.03 (d, 2H, J = 4 Hz), 7.78 (t, 2H, J = 8 Hz), 7.77 (d, 2H, J = 4 Hz), 7.15 (d, 4H, J = 8 Hz), 7.09 (d, 2H, J = 2 Hz), 7.03 (d, 2H, J = 2 Hz), 3.95 (t, 8H, J = 8 Hz), 2.70 (s, 6H), 2.56 (s, 6H), 0.75 (t, 8H, J = 8 Hz), 0.13 (m, 36H). C84H92FeN14O4Zn: m/z=1480.61, MALDI-TOF: m/z = 1626.99 [M+PF6−]+, 1481.47 [M]+.

TpyPZn (8). A 100 mL Schlenk flask equipped with a stirbar was charged with 2 (100 mg, 0.11 mmol), 7 (50 mg, 0.16 mmol), Pd(PPh3)4 (37 mg, 0.032 mmol) and CuI (6 mg, 0.032 mmol) under Ar. 40 ml THF and 4 ml diisopropylamine were mixed together and added after being degassed with 3 freeze-pump-thaw cycles. When the reaction was complete, cool it down to RT and remove the solvent. The compound was then purified by alumina chromatography (THF: hexane = 3: 7) to give a green solid (108 mg, 83%, based on 2). 1H NMR (400 MHz, CDCl3, ppm): δ 10.10 (s, 1H), 9.89 (d, 2H, J = 4 Hz), 9.26 (d, 2H, J = 4 Hz), 9.05 (s, 2H), 9.03 (d, 2H, J = 4 Hz), 8.95 (d, 2H, J = 4 Hz), 8.84 (d, 2H, J = 4 Hz), 8.74 (d, 2H, J = 8 Hz), 7.74 (t, 2H, J = 8 Hz), 7.40 (dd, 2H, J = 4 Hz), 7.05 (d, 4H, J = 8 Hz), 3.93 (t, 8H, J = 8 Hz), 0.88 (t, 8H, J = 4 Hz), 0.25 (m, 36H). C73H77N7O4Zn: m/z =1179.53, MALDI-TOF: m/z =1180.77 [M+H]+.

FeTpyPZn. A 50 mL round bottom flask equipped with a stirbar was charged with FeCl2•4H2O (3.36 mg, 0.017 mmol) in 10 ml MeCN, 9 (4.4 mg, 0.019 mmol) in 3 ml THF was added dropwise. After 5 mins, TpyPZn (20 mg, 0.017 mmol) in 7 ml THF was added. After 0.5 hr, the solution was concentrated to ~ 5 ml, and saturated KPF6 aqueous solution was added to precipitate the product. The crude product was filtered and dried. The compound was then purified by silica gel chromatography (MeCN: H2O: saturated KNO3 (aq) = 95: 4: 1). The greenish brown band was collected and evaporated to 10 ml, and saturated KPF6 aqueous solution was added to precipitate the product, which was then filtered and dried to give a FeTpyPZn as brown solid (12 mg, 40%). 1H NMR (400 MHz, CD3CN, ppm): δ 10.17 (s, 1H), 10.05 (d, 2H, J = 4 Hz), 9.53 (s, 2H), 9.30 (d, 2H, J = 4 Hz), 9.04 (d, 2H, J = 4 Hz), 8.96 (d, 2H, J = 8 Hz), 8.83 (d, 2H, J = 4 Hz), 8.76 (d, 2H, J = 8 Hz), 8.72 (t, 1H, J = 8 Hz), 8.52 (d, 2H, J = 8 Hz).
Hz), 8.00 (m, 2H), 7.91 (td, 2H, J = 8 Hz), 7.82 (d, 2H, J = 8 Hz), 7.36 (d, 2H, J = 8 Hz), 7.19 (d, 4H, J = 8 Hz), 7.14 (m, 6H), 4.00 (t, 8H, J = 8 Hz), 0.81 (t, 8H, J = 8 Hz), 0.18 (m, 36H).

C₈₈H₈₈FeN₁₀O₄Zn: m/z =1470.57, MALDI-TOF: m/z =1471.89 [M]+, 1258.84 [M−Tpy+Na]+, 1183.98 [M−Tpy−Fe+1]+

2. Instrumentation

General Characterization Instruments

A 400 MHz Brüker spectrometer was used to obtain NMR spectra for all synthesized compounds. Chemical shifts for ¹H NMR spectra are reported relative to residual protium in deuterated solvents (δ (residual) = 7.26 ppm in CDCl₃, δ (residual) = 1.94 ppm in CD₂CN, δ (residual) = 2.05 ppm in acetone-d₆, δ (residual) = 1.72 ppm in THF-d₈). All J values are reported in Hertz. Reported MALDI-TOF data were acquired with an Applied Biosystems DE-Pro MALDI-MS at the Department of Chemistry at Duke University. Samples were prepared as micromolar solutions in acetone, using HABA (2-(4-hydroxyphenylazo)benzoic acid) as the matrix. Electronic absorption spectra were acquired on a Shimadzu Pharmaspec UV-1700 spectrometer.

Electrochemistry

Cyclic voltammetry and differential pulse voltammetry (DPV) experiments were performed using a BASi EC Epsilon working station, a Ag/AgCl (3M NaCl) reference electrode, a Pt wire counter electrode, and a glassy carbon working electrode. The ferrocene/ferrocenium redox couple (0.43 V vs. SCE) was used as an internal standard.

FeNHCPZn has close-lying E₀/+= 0.76 V and E⁺/²⁺ = 0.88 V potentials (both vs. SCE, Figure S7). Here E₀/+= 0.76 V is assigned to be derived from the Fe²+/³⁺ redox pair and E⁺/²⁺ = 0.88 V is assigned to be derived from the PZn⁰+/+ redox pair, based on:

(1) The PZn⁰+/+ redox pair derived potentials in similarly structured RuPZn and FePZn are 0.87 V and 0.83 V, respectively.

(2) Both the redox potentials of FeNHCPZn and Fe(NHCPZn)₂, the homoleptic version of FeNHCPZn, have been measured by DPV and fitted by gaussian functions (Figure S7). The ratio of the fitted peak area of E⁰/+= 0.76 V and E⁺/²⁺ = 0.88 V signals is ~ 1 for FeNHCPZn; in comparison, as the ratio of (PZn moiety)/(Fe metal core) increases to 2 in Fe(NHCPZn)₂, the ratio of the fitted peak area of E⁰/+= 0.75 V and E⁺/²⁺ = 0.88 V signals becomes clearly < 1.

Ultrafast (fs-ns) Pump-probe Transient Absorption Spectroscopy

Ultrafast transient absorption spectra were obtained using standard pump-probe methods. Optical pulses (≥ 120 fs) centered at 775 nm, were generated using a Ti:Sapphire laser (Clark-MXR, CPA-2001, Dexter, MI, USA), which consisted of a regenerative amplifier seeded by a mode-locked fiber oscillator. The output of the regenerative amplifier was split to feed an optical parametric amplifier (Light Conversion Ltd., TOPAS-C, Vilnius, Lithuania), which generates excitation pulses tunable in wavelength from the UV through the NIR region. The pump beam was chopped at half the laser repetition rate (~500 Hz). A fraction (<5%) of the output from the regenerative amplifier was passed through an optical delay line, and focused onto a 3 mm c-cut sapphire plate to generate a white light continuum, which was used as the probe beam. The polarization and attenuation of the pump and probe beams were controlled by half-wave plate and Rochon prism polarizer pairs. The polarization was set to the magic angle
(54.7 °) for these experiments. The pump beam was focused into the sample cell with an \( f = 20 \) cm lens, while the probe beam was focused with a parabolic mirror. The excitation pump power was measured using a power meter (Coherent, LabMax Top with PS19 head). After passing through the sample, the probe light was adjusted using a neutral density filter to avoid saturating the detector, and focused onto the entrance slit of a computer-controlled image spectrometer (Acton Research Corporation, SpectraPro-150, Trenton, NJ, USA). A CCD array detector (1024 x 128 elements, Roper Scientific, Trenton, NJ, USA), interfaced to the spectrometer, recorded the spectrum of the probe light from the UV (~370 nm) to the NIR (~1100 nm), providing spectral resolution better than 0.5 nm. Pairs of consecutive spectra were measured with \( (I_{\text{on}}(\lambda)) \) and \( (I_{\text{off}}(\lambda)) \) to determine the difference spectrum, \( \Delta A = \log(I_{\text{off}}(\lambda)) / (I_{\text{on}}(\lambda)) \). All these experiments utilized a custom-built 2 mm-path-length fused-silica sample cell; all transient optical studies were carried out at 21 ± 1 °C in freshly distilled acetonitrile solvent. All transient spectra reported represent averages obtained over 3-5 scans, with each scan consisting of ~300 time delays spaced on a log scale, with each time delay an average of 3000 frames. In these experiments, the optical delay line utilizes a computer-controlled delay stage. Delay times up to 4 ns were achieved using a Compumotor-6000 (Parker). Following all pump-probe transient absorption experiments, electronic absorption spectra verified that the samples were robust.

**Time-Resolved Emission Spectroscopy**

Time-resolved emission data were recorded using a Hamamatsu C4780 picosecond fluorescence lifetime measurement system, which utilizes a Hamamatsu Streakscope C4334 photon counting detector, a Hamamatsu C4792-01 synchronous delay generator, and a Stanford Research Systems DG535 electronic delay generator. FeNHCPZn was excited by a Hamamatsu PLP-10 laser diode (405 nm), and the polarization of emission was set to the magic angle (54.7 °) for these experiments. Hamamatsu HPD-TA software was used to acquire emission data in the single-photon counting mode, and its fitting module was used to fit the emission lifetime by deconvolution with the experimentally determined instrument response function (irf). The irf was measured using a scattering sample (cream or silica dispersed in water). Sample concentrations were adjusted to give an optical density of ~0.1 at the excitation wavelength.

**DSSC Device Configuration Photocurrent–Photovoltage Measurements**

SnO\(_2\) nanoparticle-coated FTO glass substrates were prepared using established methods\(^7\). N\(_3\) dye-loaded SnO\(_2\)/FTO photoelectrodes were prepared by immersing the SnO\(_2\)/FTO slide in an ethanol solution containing 0.5 mM N\(_3\) [bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II)]\(^8\) for 24 h. The FeNHCPZn-sensitized photoelectrode (FeNHCPZn/SnO\(_2\)/FTO) was prepared by immersing an SnO\(_2\)/FTO slide in ethanol solution containing 1 mM pyridine-4-carboxylic acid for 24 h, following which it was exposed to an ethanol solution containing 0.5 mM FeNHCPZn (24 h). After drying the FeNHCPZn/SnO\(_2\)/FTO under a N\(_2\) stream, a simplified regenerative cell was assembled with this photoelectrode using a Pt wire as the cathode and an acetonitrile electrolyte solution containing 0.5 M tetra-n-butylammonium iodide and 0.05 M I\(_2\). Photocurrent–photovoltage (J–V) responses were measured using a Newport Oriel 92192 solar-simulated light source (AM 1.5G filtered, 100 mW cm\(^{-2}\)) with a Keithley 2400 source meter. The active cell areas in these devices were typically 0.5 cm\(^2\).
3. Electronic Absorption and Pump-probe Spectra of NHC-ethyne-PZn

The electronic absorption spectrum of NHC-ethyne-PZn is shown in Figure S9. Without the presence of Fe(II) metal core, the MLCT derived band of FeNHCPZn that is centered ~ 516 nm is absent in the spectrum of NHC-ethyne-PZn. Moreover, the NHC-ethyne-PZn B-derived band (FWHM = 1437 cm\(^{-1}\), that of TIPS-E-PZn is 662 cm\(^{-1}\)) is much narrower than the B-derived band of FeNHCPZn(FWHM = 2279 cm\(^{-1}\)), due to the smaller extent of CT character without mixing with Fe complex derived MLCT state.

Unlike the pump-probe transient absorption spectra of FeNHCPZn, the spectra of NHC-ethyne-PZn (Figure S10) do not present prominent NIR signals in 700~1100 nm spectral range. Only at a longer delay time on ns scale, the rise of a very weak NIR band centered ~ 770 nm is detected along with the signal rise at ~530 nm with \(\tau = 3.2\) ns. This excited absorption feature resembles that of porphyrin monomers and the 3.2 ns time constant is typical of porphyrin monomers ISC time constant.

The comparison of FeNHCPZn and NHC-ethyne-PZn excited state absorption features indicates that while NHC-ethyne-PZn excited states mainly exhibit porphyrin-derivated \(\pi-\pi^*\) character, the excited states of FeNHCPZn evince new features as a result of extensive excited state mixing between building-block chromophoric moieties.

4. Excited-state Redox Potentials

The redox potentials of FeNHCPZn and Fe(NHC)\(_2\) electronically excited states are calculated from respective \(E_{0,0}\) energies and ground state redox potentials.\(^{15}\)

The \(T_1\) state \(E_{0,0}\) energy of FeNHCPZn is estimated from the \(3^\text{CT}\) emission energy corresponding to 10% intensity of that of the highest energy emission maximum (the “10% rule”), assuming a Gaussian emission shape.\(^{16-17}\) Thus, the \(T_1\) state \(E_{0,0}\) energy of FeNHCPZn is estimated as 1.53 eV.

\[3E(\text{FeNHCPZn})^{\ast/\ast} = E(\text{FeNHCPZn})^{0/\ast} - 3E_{0,0} = 0.76 - 1.53 = -0.77\text{ V} \quad (\text{Eq. S1})\]

5. A proof of principle DSSC architecture that exploits FeNHCPZn

Figure S12 highlight the utility of FeNHCPZn as a DSSC photosensitizer in a regenerative cell architecture that exploits a FeNHCPZn-sensitized photoelectrode (FeNHCPZn/SnO\(_2\)/FTO). In this photoelectrode, the FeNHCPZn molecules are anchored via pyridine-4-carboxylic acid, which simultaneously coordinates the zinc ion of the supermolecule and binds the SnO\(_2\) semiconductor surface (Figure S12A). Figure S12B displays the photocurrent-photovoltage (J-V) response of this regenerative cell: the short-circuit current (JSC) and open-circuit voltage (\(V_{oc}\)) of this system were determined to be 1.25 mA/cm\(^2\) and 0.18 V respectively, under AM 1.5 G light (performance without optimization). Note that the photocurrent derived from the SnO\(_2\)/FTO photoelectrode is negligible (Figure S12C), underscoring that electron injection in the FeNHCPZn/SnO\(_2\)/FTO photoelectrode derives from FeNHCPZn absorption. While no attempt was made to optimize device performance, we note that an identical cell that featured a chromophore/SnO\(_2\)/FTO photoanode and exploited the benchmark N3 dye gave rise to \(J_{SC} = 2.1\) mA/cm\(^2\) and \(V_{OC} = 0.32\) V, when examined under identical conditions.

6. Computational Details
All structures were optimized using selected DFT functionals (M06L, B3LYP, and TPSSh) with the polarizable continuum model (acetonitrile) as implemented in Gaussian 16 A03. The def2-SVP basis set was employed for C, N, O and H atoms, and the Lanl2DZ ECP basis was used for the Zn atom. For the Fe atom, we employed a small core relativistic pseudopotential ECP10MDF along with a valence (8s7p6d2f1g)/[6s5p3d2f1g] basis set. Empirical dispersion corrections were used in all the DFT calculations: D3BJ for B3LYP, and TPSSh and D3 for M06L. The stability of the DFT wave function was checked for all the optimized structures. DFT results were further verified by the domain-based local pair natural orbital coupled cluster (DLPNO-CCSD(T)) theory as implemented in the ORCA 4.2.1 quantum chemistry package. DLPNO-CCSD(T) is designed to reproduce approximately 99.9% of the canonical correlation energy and aims to deliver results of “gold-standard” quality. The DLPNO-CCSD(T) computations were performed using the def2-SVP basis set for all atoms with the NormalPNO threshold and the CPCM model that simulates the solvent effects. The DFT computed relative energies of the quintet and triplet states are consistent with the CCSD(T) predictions and agree closely with experiments.

As shown in Figure S1, the FeNHCPZn Q state has a mixed character of charge transfer and local excitation. Thus, the low energy $^5$MC electronically excited state common to traditional Fe coordination complexes such as Fe(tpy)$_2$ appears as a higher lying quintet state in FeNHCPZn. This FeNHCPZn Q state manifests both $^5$MC and CT transition character that involves the conjugated extended ligand, due to the extensive degree of configuration interaction that describes the electronically excited states of this supermolecule.
Figure S1. The synthetic route to FeNHCPZn. (i) Pd$_2$(dba)$_3$, AsPh$_3$, diisopropylamine, THF, 0 °C to RT; (ii) CuI, Cs$_2$CO$_3$, DMSO, 90 °C; (iii) Me$_3$OBF$_4$, dry DCM, RT; (iv) t-BuOK, THF, −78°C, anhydrous FeBr$_2$. (All charged compounds feature PF$_6^-$ counterions.)

Figure S2. The synthetic route of FeTpyPZn. (i) Pd(PPh$_3)_4$, CuI, diisopropylamine, THF, 60 °C; (ii) FeCl$_2$•4H$_2$O, MeCN, THF, RT. (All charged compounds contain PF$_6^-$ as counter ions.)
Figure S3. The aromatic region of the $^1$H NMR spectrum of FeNHCPZn recorded in CD$_3$CN solvent.

Figure S4. The aromatic region of $^1$H NMR spectrum of FeTpyPZn in CD$_3$CN.
Figure S5. The MALDI-TOF mass spectrum of FeNHCPZn.

Figure S6. The MALDI-TOF mass spectrum of FeTpyPZn.
Figure S7. (Top) Potentiometric data of FeTpyPZn and FeNHCPZn (vs. SCE) in 0.1 M TBAPF$_6$/acetonitrile electrolyte/solvent system. Red line represents data from cyclic voltammetry. Green line represents data from differential pulse voltammetry. (CV data were only used to show the number of peaks and only DPV data was used for obtaining redox potential values). (Middle) Fitting of FeNHCPZn DPV signals with gaussian functions. (Bottom) Fitting of Fe(NHCPZn)$_2$ DPV signals with gaussian functions.
Figure S8. Electronic absorption spectra of Fe(tpy)$_2$, Fe(NHC)$_2$, FePZn, and FeNHCPZn in acetonitrile solvent (top) and total integrated absorptive oscillator strengths calculated over the 28571 cm$^{-1}$ (350 nm) to 13333 cm$^{-1}$ (750 nm) spectral range (bottom).

Figure S9. Electronic absorption spectrum of the NHC-ethyne-PZn ligand in MeCN.
Figure S10. Representative ultrafast pump-probe spectra recorded at several time delays and representative kinetic traces at different probe wavelengths for the NHC-ethyne-PZn ligand in MeCN ($\lambda_{\text{ex}} = 640$ nm; $P_{\text{ex}} = 310$ μW).
Figure S11. 2D-plot of FeNHCPZn pump-probe spectra recorded in (a) MeCN and (b) dioxane solvents. (The T₁→Tₙ transition band maximum in dioxane solvent redshifts ~330 cm⁻¹ relative to that observed in MeCN while the S₁→Sₙ transition band maximum redshifts only ~10 cm⁻¹.)
Figure S12. Utility of FeNHCPZn as a DSSC photosensitizer in a regenerative cell architecture. (A) Schematic diagram of the DSSC architecture that exploits the FeNHCPZn/SnO$_2$/FTO photoelectrode. (B) J–V responses obtained under dark and AM 1.5 G illumination. (C) J–V response of an identical cell incorporating a bare SnO$_2$/FTO photoelectrode. Experimental conditions: AM 1.5 G light, 0.5 M TBAI, 0.05 M I$_2$, MeCN, Pt wire counter electrode, active cell area of ~0.5 cm$^2$. 
Figure S13. (a) Representative pump-probe spectra recorded at various delay times for FeNHCPZn on SnO$_2$ surfaces ($\lambda_{ex} = 640$ nm, $P_{ex} = 430$ μW). (b) Excited state decay dynamics of FeNHCPZn in MeCN solvent (from Fig. 3B, grey – raw data; blue – kinetic fit) and on SnO$_2$ (green – raw data; red – kinetic fit) at ~915 nm representative probe wavelength. For FeNHCPZn on SnO$_2$, the amplitudes associated with the two ultrafast decay time constants $\tau_1 \sim 0.07$ ps ($A_1 \sim 56\%$) and $\tau_2 \sim 2$ ps ($A_2 \sim 27\%$) indicate ~80% of the total injected charge from the FeNHCPZn $^3$MLCT state following optical excitation; these two ultrafast decay time constants mirror the established electron injection time constants characteristic of Ru(II) complexes anchored on TiO$_2$ and SnO$_2$ surfaces.\textsuperscript{18-19}
**Figure S14.** J–V response for an identical cell that featured a chromophore/SnO$_2$/FTO photoanode based on the benchmark N$_3$ dye. Experimental conditions: AM 1.5G light, 0.5 M TBAI, 0.05 M I$_2$, MeCN, Pt wire counter electrode, active cell area of ~0.5 cm$^2$.

**Figure S15.** The four B3LYP-computed SOMOs of FeNHCPZn Q$_1$ state. These orbitals show that the quintet state has a mixed character of charge transfer and local excitation. SOMO energies increase in the order: SOMO(A) < SOMO(B) < SOMO(C) < SOMO(D).
Table S1. Distances (Å) between the iron and ligand atoms at the B3LYP-optimized minima on the computed S₀, T₁, and Q₁ potential energy surfaces. The ligand atom ordering is the same for FeNHCPZn and FePZn.

|       | FeNHCPZn |       | FePZn |
|-------|----------|-------|-------|
|       | S₀       | T₁    | Q₁    | S₀     | T₁    | Q₁    |
| Fe-N₁ | 1.934    | 1.910 | 1.924 | Fe-N₁  | 1.900 | 1.927 | 2.093 |
| Fe-C₂ | 1.961    | 1.971 | 1.975 | Fe-N₂  | 1.999 | 2.137 | 2.212 |
| Fe-N₃ | 1.939    | 1.954 | 1.944 | Fe-N₃  | 1.903 | 1.929 | 2.117 |
| Fe-C₄ | 1.961    | 1.984 | 1.999 | Fe-N₄  | 1.999 | 2.137 | 2.212 |
| Fe-C₅ | 1.961    | 1.971 | 1.984 | Fe-N₅  | 1.998 | 2.130 | 2.181 |
| Fe-C₆ | 1.961    | 1.984 | 1.984 | Fe-N₆  | 1.997 | 2.130 | 2.181 |

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