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Triplet State Formation in Homo- and Heterometallic Diketopyrrolopyrrole Chromophores

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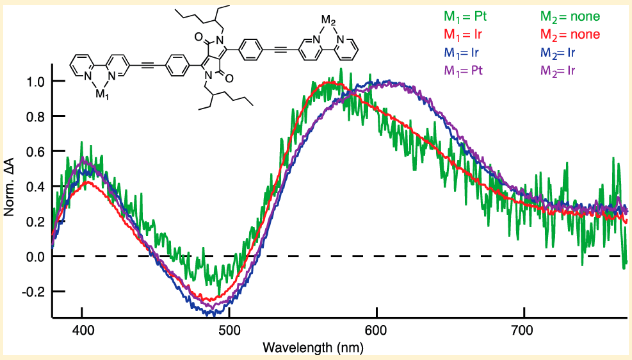
S *Supporting Information*

ABSTRACT: The synthesis, structural characterization, and excited-state dynamics of series of diketopyrrolopyrrole (DPP) bridged homodinuclear Ir(III) and heterodinuclear Ir(III)/Pt(II) complexes is described. Steady-state and time-resolved photoluminescence along with transient absorption measurements were used to probe the nature of the emissive and long-lived excited states. Upon excitation into the ^{1}DPP ligand-localized excited state in the presence of coordinated Ir(III) or Pt(II) metal centers, the intersystem crossing is enhanced, leading to a quenching of the ^{1}DPP fluorescence and the formation of the long-lived ($\tau \approx$ 30–40 μs) ^{3}DPP excited state in all instances.



INTRODUCTION

Diketopyrrolopyrrole (DPP) dyes represent an interesting class of light-harvesting chromophores, which are utilized as both small molecules and in polymeric forms for their high fluorescence quantum efficiencies in diverse areas such as photorefractive materials,[1] fluorescence sensors,[2] thin film transistors,[3] and light-emitting diodes.[4,5] These robust dyes have also emerged as promising candidates for low-cost photovoltaics based on organic bulk heterojunctions[6−12] as well as dye sensitization schemes.[13−15] We recently discovered that modification of the central DPP core with lateral triazatruxene groups leads to exceptional photon-to-current conversion in solution-processed solar cells.[16] The optical and redox properties of DPP dyes can be easily tuned through modification of the appended aromatic rings, which makes them well-suited for sunlight capture and energy conversion applications.[17−20] Similarly, given that triplet excitons can be used to enhance photovoltaic performance in a variety of next-generation devices,[21] the question of how one might access the triplet excited states of DPP dyes in a facile manner is apparent.

The covalent linking of transition metal complexes to organic fluorophores such as pyrene,[22−28] boron dipyrromethenes,[29−35] perylenediimides,[36−41] and DPP[42] represents an interesting strategy to enhance intersystem crossing (ISC) to the triplet state of these appended organic chromophores. This technique of generating long-lived organic triplet states has been applied in the generation of singlet oxygen for photodynamic therapy[43] in addition to electron transfer to generate a charge-separated species.[44] This latter process is crucial to the performance of bulk heterojunction solar cells, wherein charge separation followed by charge collection at select electrodes produces electrical photocurrent.[45,46]

Cyclometalated Ir(III) complexes are convenient to prepare, synthetically versatile, photochemically stable, and display desirable photophysical properties.[47−49] Many interesting applications, such as sensing and bioimaging,[50,51] organic light-emitting devices,[52−56] and sensitized photon upconversion,[57] have been developed for this family of complexes. Similarly, square planar Pt(II) complexes are also very popular for their exceptional spectroscopic properties such as long-lived triplet exited states, high phosphorescence quantum yields, and emissive properties prone to be sensitive to the environment.[58−61]

This present paper builds upon our previous work with Ir(III)-substituted DPP chromophores.[42] In this previous contribution, the symmetric coordination of two cyclometalated Ir(III) chromophores produced long-lived DPP localized triplet states in two distinct DPP bridging ligand frameworks. In the present work we explore the effect that the number and identity of coordinated heavy metals has on the photophysics of the DPP chromophore. The complexes were constructed from a central DPP core equipped with two lateral 2,2′-bipyridine ligands selectively complexed with two Ir(III) centers, one Ir(III), and one Pt(II) center, or a single Ir(III) or Pt(II) metal center. In all cases the internal heavy atoms facilitated triplet state production and produced long-lived DPP-centered triplet states as evidenced from steady-state and

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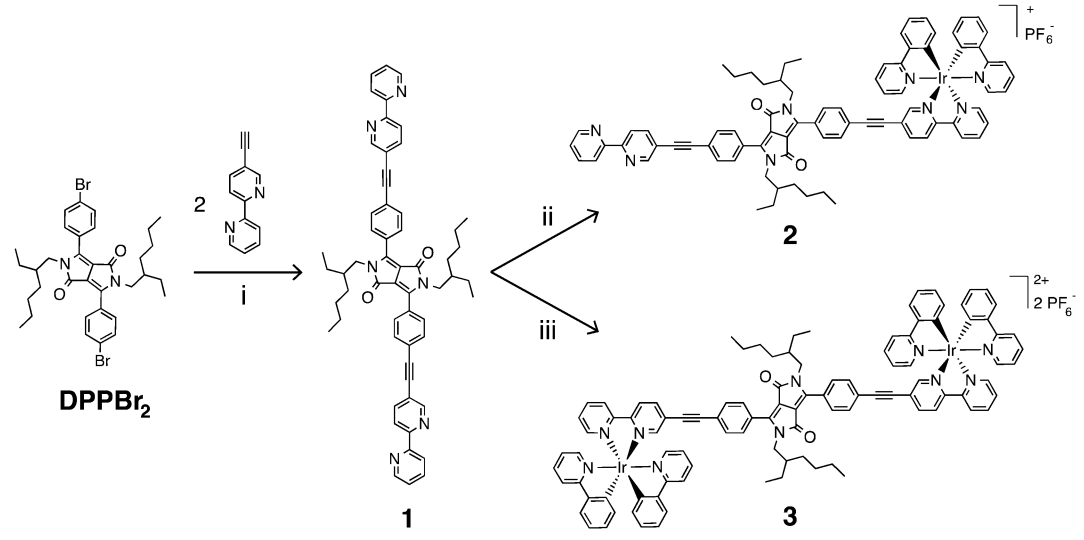
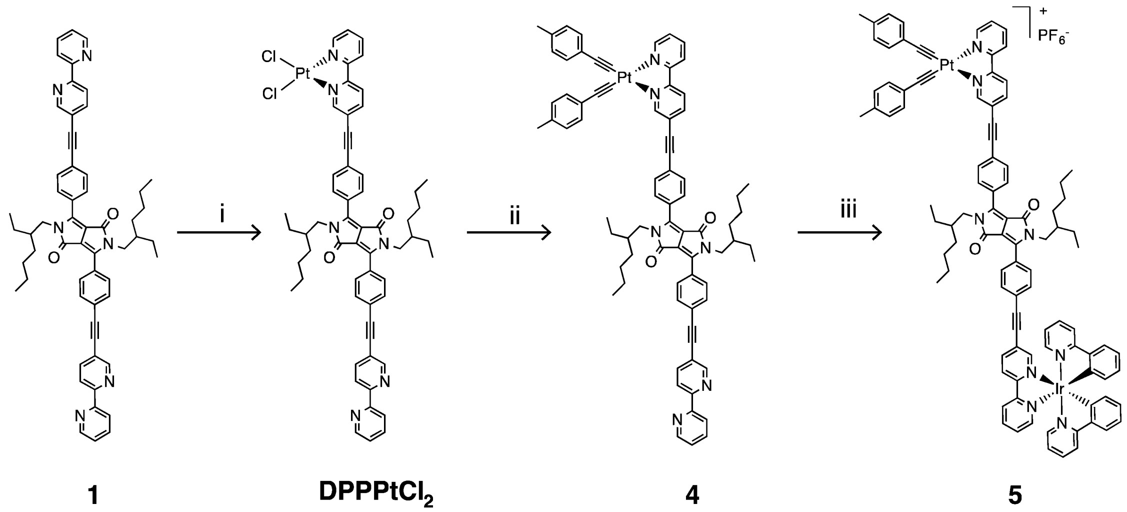
Scheme 1. Synthetic Scheme for Ligand 1 and Complexes 2 and 3[a]



[a](i) Benzene, triethylamine, [Pd(PPh$_3$)$_4$] (5.6 mol %), 60 °C, 75%. (ii) [Ir(ppy)$_2$Cl]$_2$ (0.5 equiv), dichloromethane/methanol, 80 °C, 69%. (iii) [Ir(ppy)$_2$Cl]$_2$ (2 equiv), dichloromethane/methanol, 80 °C, 88%.

Scheme 2. Synthetic Scheme for Pt-Containing Complexes 4 and 5[a]



[a](i) THF, Pt(DMSO)$_2$Cl$_2$ (1 equiv), 60 °C, 86%. (ii) Tolylacetylene, CuI (catalyst), DMF/THF/TEA, RT, 87%. (iii) [Ir(ppy)$_2$Cl]$_2$ (0.5 equiv), dichloromethane/methanol, 60 °C, 44%.

time-resolved photoluminescence as well as transient absorbance spectroscopy.

■ RESULTS AND DISCUSSION

Synthesis. The preparation of the ditopic ligand **1** and complexes **2** and **3** is presented in Scheme 1. Double cross-coupling of 3,6-bis(4-bromophenyl)-2,5-bis(2-ethylhexyl)-pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (DPPBr$_2$)[62] with 5-ethynyl-2,2′-bipyridine[63] in the presence of palladium(0) and mild reaction conditions afforded the ditopic ligand DPPbpy$_2$ (**1**) in 75% yield. Reaction of this ditopic ligand with excess [Ir(ppy)$_2$Cl]$_2$ (ppy = 2-phenylpyridine)[64] in polar solvent provided, after anion metathesis and column chromatography, [DPPIr$_2$](PF$_6$)$_2$ (**3**) in 88% yield. The use of substoichiometric amounts of the same iridium dimer under dilute conditions forms the mononuclear [DPPIr](PF$_6$) complex (**2**) in 69% yield. The more polar **3** and unreacted ligand **1** were isolated as side products in 16% and 10% yields, respectively.

The syntheses of the platinum and mixed Pt/Ir complexes are depicted in Scheme 2. Unfortunately, the mixed Pt/Ir complex could not be synthesized starting from **2** because an intractable mixture of products was formed. The reaction of stoichiometric amounts of Pt(DMSO)$_2$Cl$_2$[65] (DMSO = dimethyl sulfoxide) with **1** yielded the DPPPtCl$_2$ complex, which precipitated out of the reaction mixture during the course of the reaction and could be isolated in 86% yield. In a second step both chloride ligands are substituted with tolylacetylene under anaerobic conditions in the presence of catalytic amounts of CuI to form DPPPt (**4**) in 87% yield. Finally, reaction of the [Ir(ppy)$_2$Cl]$_2$ dimer with **4** yields the heterodinuclear [DPPPtIr](PF$_6$) (**5**) in 44% yield.

The present synthetic approach differs markedly from that used for the preparation of **3** in our previous account.[42] In that work a $[Ir(ppy)_2(bpy)]^+$ precursor bearing an ethynyl−bipyridine ligand was cross-linked directly to the $DPPBr_2$ precursor forming the desired $[DPPIr_2](PF_6)_2$ in a single step. The use of similar Pt(II) ethynyl−bipyridine complexes was not investigated in this work due to the high reactivity of the ethynyl−bipyridine ligand toward the Pt(II) center in the presence of specific catalysts. Furthermore, it proved impossible to control the mono cross-coupling reaction of a single $[Ir(ppy)_2(ethynyl\text{-}bpy)]^+$ complex on the $DPPBr_2$ platform. The best strategy, highlighted herein, is to complex first the ditopic ligand with a single Pt center, followed by postfunctionalization of the platinum center with the suitable alkynyl substituents, and finally Ir(III) complexation on the free bpy coordination site. All complexes were fully characterized by NMR, electrospray ionization mass spectrometry (ESI-MS), elemental analysis, and spectroscopic techniques allowing the unambiguous assignment of their molecular structure.

Steady-State Spectroscopy. The photochemical stability and photophysical properties of **1**−**5** are very sensitive to the presence of oxygen. Reproducible ground- and excited-state absorption spectra in addition to excited-state lifetimes with minimal photochemical decomposition could only be obtained when compounds were stored in an inert atmosphere glovebox and spectroscopic samples were prepared in an inert atmosphere glovebox filled with N_2. The normalized absorption and photoluminescence spectra of **1**−**5** are shown in Figure 1.

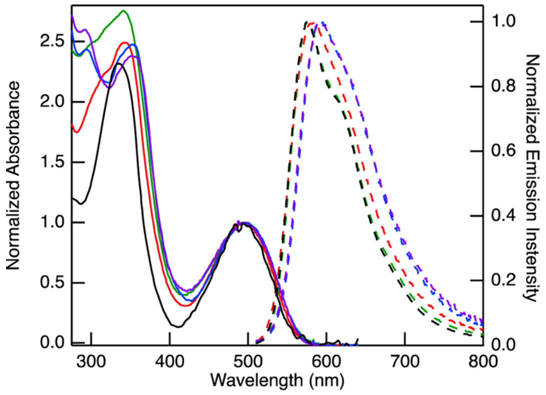


Figure 1. Normalized absorption (solid) and emission (dashed) spectra of **1** (black), **2** (red), **3** (blue), **4** (green), and **5** (purple) in acetonitrile solution.

The intraligand (IL) absorption bands of the DPP chromophore dominate the absorption spectra of all five complexes both in the visible (495 nm) and UV (~335 nm) regions (Figure 1). The coordination of the ethynyl−bipyridine groups to the DPP does lead to a significant red shift in the visible absorption band relative to the previously reported $DPPBr_2$[42] due to extended π conjugation (Figure 1). Interestingly, the identity and number of metals coordinated to the bipyridyl ligands has no significant, additional effect on the absorption spectrum. The emission spectra of the five complexes are similar in shape, with the Ir(III)-coordinated complexes (**2**, **3**, and **5**) being slightly red-shifted and less structured. The complexes with two coordinated metals (**3** and **5**) show the most significant red-shifted spectra and are superimposable with each other. This is most likely due to the increased (and more symmetric) delocalization in the lowest unoccupied molecular orbital (LUMO) of the doubly coordinated complexes compared to the singly coordinated complexes or free ligand, as shown in the calculated structures in Figure 2. The uncoordinated **1** is highly fluorescent (QY = 77.3%), which is consistent with unquenched fluorescence from DPP. The DPP-based fluorescence in the metal-coordinated complexes is quenched relative to **1**, with the Ir(III)-containing complexes being nearly quantitatively quenched (Table 1). The fluorescence intensity of **4** was also noticeably reduced relative to **1**, but the presence of free (unquenched) **1**, determined by time-resolved emission, made it impossible to determine the true quantum yield of **4**. NMR analysis of **4** (Supporting Information, Figures S12−S13) showed no detectable trace of uncoordinated **1**. This fact, coupled with the very poor solubility of **1** in acetonitrile, suggests that **1** is a decomposition product of **4** in solution rather than being present in the purified solid. As was shown previously, the presence of heavy metals enhances the ISC to the DPP-localized triplet state, quenching the fluorescence intensity.[42]

As shown previously for **3**,[42] triplet state formation in **2**, **4**, and **5** was also confirmed by $^1O_2$ sensitization (Figure 3). The complexes were dissolved in aerated acetonitrile, and the phosphorescence of $^1O_2$ at 1275 nm was recorded under 500 nm Xe lamp excitation. While the formation of $^1O_2$ could be qualitatively established, the yield of $^1O_2$ formation could not be determined due to the unfortunate photodecomposition of these metal−organic chromophores in the presence of oxygen.

Figure 4 presents the low-temperature emission spectra of **2**−**5** collected at 77.2 K in an optical glass formed from a 9:2 mixture of butyronitrile and propionitrile. In the visible region, the fluorescence shifts to lower energy in the frozen solution and remains short-lived (Supporting Information, Figure S3). This is additional evidence that the fluorescent state is not charge transfer in character, which typically exhibits a significant rigidochromic blue shift. No phosphorescence signal could be detected in the red or near-infrared (NIR), and the red-shifted (and intensified) visible fluorescence tails into the NIR region and simply overwhelms any potential phosphorescence signal.

Time-Resolved Spectroscopy. The emission lifetimes of **1**−**5** were measured by time-correlated single-photon counting spectroscopy and are collected in Table 1 and Supporting Information, Figure S4. The emission lifetime of **1** is 4.6 ns, which is consistent with fluorescence from the ^1IL state of the DPP chromophore. The lifetimes of **2**, **3**, and **5** were too short to be resolved (<200 ps), which is not surprising given their highly quenched steady-state emission intensities. The lifetime of **4** is biexponential, with a < 200 ps component and a 4.6 ns component of approximately equal amplitude. This biexponential emission decay suggests that **1** is also present in solution, as discussed above. This result also explains why the steady-state emission spectra of **4** and **1** are superimposable.

Transient absorption spectroscopy performed on **2**−**5** all demonstrate the formation of a long-lived triplet excited state (Figure 5). The transient difference spectra of all four complexes are nearly identical, all matching the ^3DPP difference spectra previously reported for **3**.[42] The monocoordinated **2** and **4** are slightly longer-lived (36−38 μs) with a blue shift in the transient absorption difference feature at ~600 nm. The bis-coordinated **3** and **5** have somewhat shorter-lived transient absorption decays (29 μs) but a very similar transient difference spectrum. The observed transient absorption decay time of **3** is much longer than what was previously reported due to storing and preparing the sample in an inert atmosphere glovebox in the present investigation.

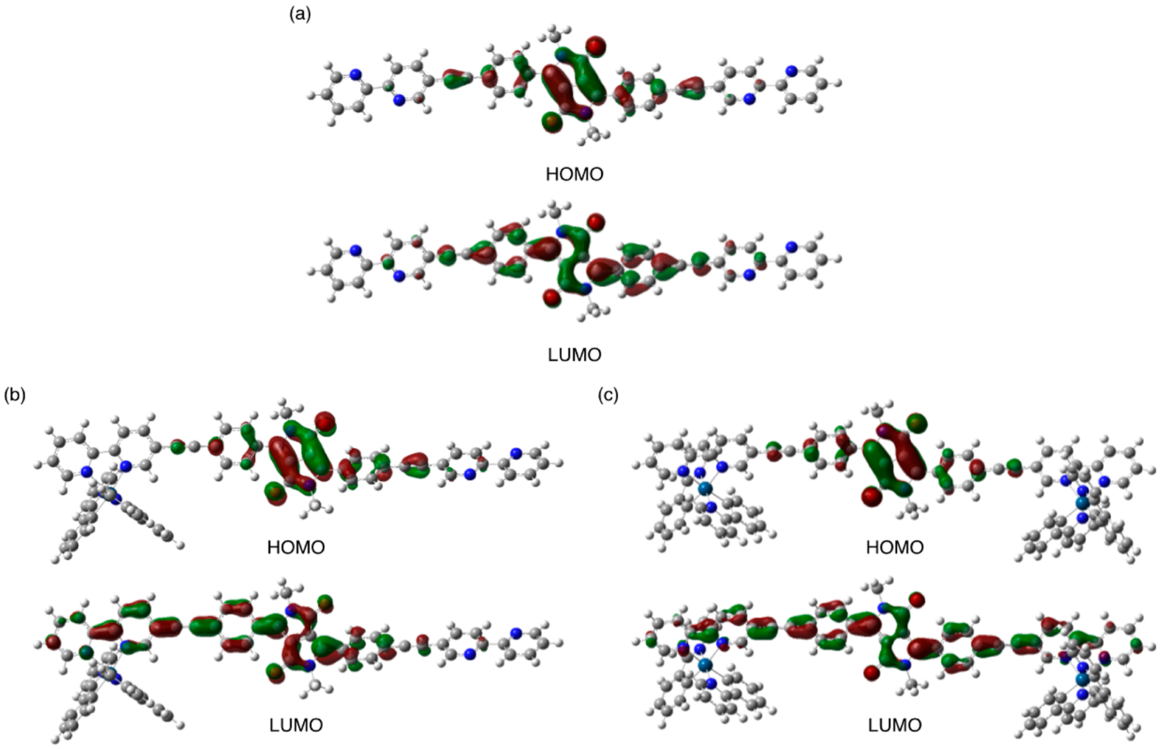


Figure 2. DFT-calculated isodensity plots of the HOMO and LUMO orbitals of the geometry-optimized ground states of (a) **1**, (b) **2**, and (c) **3** in an acetonitrile dielectric continuum.

Table 1. Photophysical Properties of Ditopic Ligand 1 and Metallochromophores 2–5[a]

complex	λ_{abs} (nm)	λ_{em} (nm) RT	λ_{em} (nm) 77 K[b]	ϕ (%)	τ_{em} (ns)	τ_{TA} (μs)
1	273, 335, 494	575	*c*	77.3[d]	4.6	*e*
2	253, 344, 495	582	641	0.4[f]	<0.2	36.3
3	252, 294, 353, 496	591	611	0.4[f]	<0.2	29.2
4	342, 498	575	624	*g*	4.6, <0.2[h]	38.7
5	265, 292, 352, 496	591	641	0.3[f]	<0.2	29.2

[a] Measured in acetonitrile solution. [b] Measured in a 9:2 mixture of butyronitrile and propionitrile at 77.2 K. [c] Not sufficiently soluble in 9:2 butyronitrile and propionitrile. [d] Absolute quantum yield (±3%). [e] No detectable transient absorption signal. [f] Measured relative to $[Ru(bpy)_3](PF_6)_2$ in aerated acetonitrile ($\Phi = 0.018$) (±10%).) [g] Could not be determined due to trace amounts of **1** in solution. [h] Biexponential emission decay.

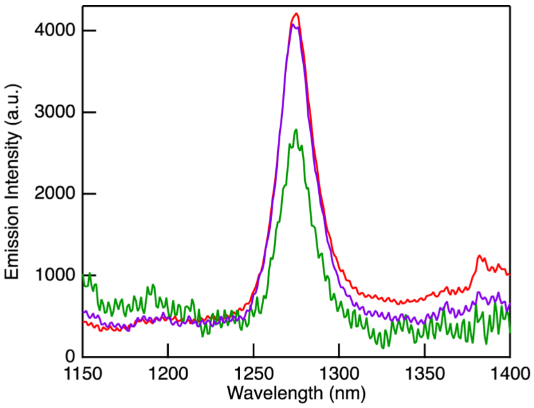


Figure 3. Phosphorescence of $^1O_2$ sensitized by **2** (red), **4** (green), and **5** (purple) in aerated acetonitrile solutions. Phosphorescence intensities are corrected for differences in absorbance at the excitation wavelength (500 nm).

■ CONCLUSIONS

This paper expands on our previous study related to Ir(III)-coordinated diketopyrrolopyrrole chromophores.[42] In that work symmetric coordination of Ir(III) chromophores to two different DPP frameworks resulted in the formation of long-lived, DPP-based triplet states thereby illustrating how the photophysics of the DPP chromophore can be substantially altered as a result of imposing this structural motif. The present contribution includes detailed photophysical investigations on a number of newly synthesized homo- and heterobimetallic DPP-based chromophores featuring coordination of Ir(III) and Pt(II) metal centers in all possible combinations. The bpy–DPP–bpy linker resulted in DPP chromophores exhibiting extended π-conjugation and substantially red-shifted absorption and fluorescence spectra resulting from coordination-induced planarization on both ends of the molecule. The singlet-state photophysics normally associated with the DPP moiety as featured in **1** becomes largely transformed into triplet-state dominated photophysics in the metal–organic assemblies **2–5**, as evidenced by strong singlet-state quenching, the generation of long-lived absorption transients, and the sensitization of $^1O_2$ photoluminescence. This current work illustrates that the identity and number of coordinated heavy metals, at least in the cases of Ir(III) and Pt(II), do not appear to represent an important design criterion in determining triplet-state formation from the DPP subunit or its subsequent excited-state decay. The presence of either a single Ir(III) or Pt(II) center or the combination of both Ir(III) and Pt(II) all lead to the

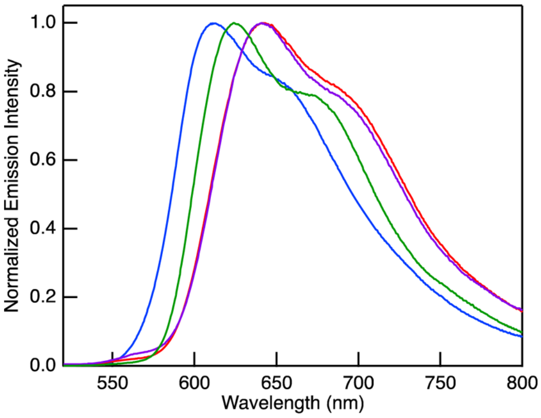


Figure 4. Normalized low-temperature emission spectra of **2** (red), **3** (blue), **4** (green), and **5** (purple) collected at 77.2 K in a 9:2 mixture of butyronitrile and propionitrile.

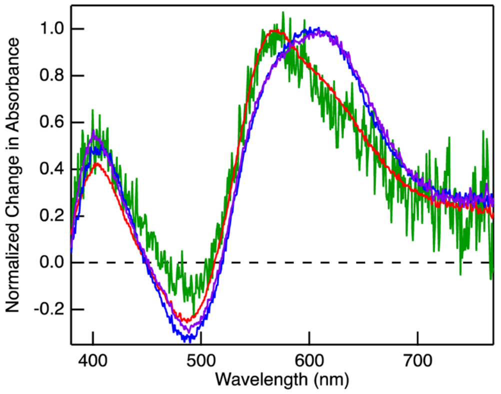


Figure 5. Normalized transient absorption difference spectra of **2** (red), **3** (blue), **4** (green), and **5** (purple) measured in air-free acetonitrile solution.

formation of a long-lived (∼30−40 μs) DPP-centered triplet excited state. The long-lived triplet excited state of the DPP-based ligand is universally sensitized in all of the metalated chromophores reported herein, enabling significant exciton diffusion in organic-based photovoltaics as well as making the current molecules susceptible to bimolecular chemistry necessary in transformations relevant to solar fuels photochemistry and potentially in the photochemical synthesis of organic molecules.

■ EXPERIMENTAL SECTION

Note. No hazardous chemicals were used during these syntheses. All solvents must be maintained and manipulated under well-ventilated hoods.

General Methods. ^{1}H and ^{13}C NMR spectra were recorded at room temperature (RT) on 300 or 400 MHz spectrometers. Chemical shifts are given in ppm and are referenced to residual solvent signals. Elemental analyses were performed with a Thermo Finnigan Flash EA 1112 Series. Mass spectrometry by electrospray ionization (ESI) was obtained with an Agilent 6210 Time-of-Flight LC/MS. Chromatographic purification was conducted using 40−63 μm silica gel or aluminum oxide 90 standardized. Thin layer chromatography (TLC) was performed on silica gel or aluminum oxide plates coated with fluorescent indicator. All mixtures of solvents are given in v/v ratio. All anhydrous reactions were carried out under dry argon using Schlenk tube techniques. $DPPBr_2$,[62] 5-ethynyl-2,2′-bipyridine,[63] $[Ir(ppy)_2Cl]_2$,[64] and $Pt(DMSO)_2Cl_2$[65] were synthesized according to reported literature procedures.

Syntheses of 3,6-Bis(4-(2,2′-bipyridin-5-yl-ethynyl)phenyl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (DPPbpy$_2$, 1). To a degassed solution of $DPPBr_2$ (249.6 mg, 0.3722 mmol) and 5-ethynyl-2,2′-bipyridine (149.1 mg, 0.827 mmol) in a mixture of benzene (20 mL) and triethylamine (5 mL) was added $Pd(PPh_3)_4$ (23.9 mg, 0.0207 mmol). The reaction mixture was heated to 60 °C for 2 d. The reaction was then cooled to RT and concentrated under reduced pressure. The crude residue was washed with water (30 mL) and brine (30 mL) and then extracted with dichloromethane (3 × 30 mL), dried over $MgSO_4$, and filtered. The solvent was evaporated to dryness, and the residue was purified on flash silica gel (static phase) eluting with dichloromethane and then dichloromethane/EtOH (gradient from 99.5:0.5 to 98:2) as mobile phase to give **1** (242.9 mg, 75%). Finally, this compound was recrystallized by evaporation of a solution EtOH/dichloromethane to afford 214.2 mg (0.246 mmol, 66%) of **1** as yellow powder. ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 8.83 (d, *J* = 1.8 Hz, 2H), 8.69 (d, *J* = 4.6 Hz, 2H), 8.43 (d, *J* = 8.0 Hz, 4H), 7.97 (dd, ^3J = 8.1 Hz, ^4J = 2.2 Hz, 2H), 7.88−7.77 (m, 2H), 7.76 (dd, ^3J = 40.3 Hz, ^4J = 8.4 Hz, 8H), 7.33 (dd, ^3J = 7.2 Hz, ^4J = 5.2 Hz, 2H), 3.69−3.84 (m, 4H), 1.22−1.32 (m, 2H), 0.98−1.23 (m, 16H), 0.81 (t, *J* = 6.6 Hz, 6H), 0.73 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$), δ (ppm): 162.64, 155.41, 155.13, 151.80, 149.31, 148.15, 139.48, 136.95, 131.97, 128.91, 128.49, 125.33, 123.97, 121.50, 120.40, 119.94, 110.17, 93.19, 89.17, 77.36, 45.08, 38.57, 30.46, 28.39, 23.88, 23.00, 14.06, 10.55. ESI-MS (dichloromethane/methanol, 50/50 + 0.1% trifluoroacetic acid) positive mode of analysis: 869.3 ([M + H], 100). Anal. Calcd for $C_{58}H_{56}N_6O_2$: C, 80.15; H, 6.49; N, 9.67; Found: C, 79.85; H, 6.11; N, 9.42%.

$[DPPIr_2](PF_6)_2$ (3). To a solution of **1** (24.0 mg, 0.0276 mmol) in dichloromethane (2 mL) was added MeOH (2 mL) and $[Ir(ppy)_2Cl]_2$ (59.2 mg, 0.0552 mmol). The reaction mixture was heated to 80 °C for 3 d. This mixture was cooled to RT, and a yellow precipitate was formed. This precipitate was isolated by filtration over paper. The crude solid was dissolved in a minimum of dimethylformamide (DMF) (2 mL). This solution was added slowly to a stirred solution of KPF_6 (60 equiv, 300 mg) in water (2 mL), and an orange precipitate formed. This precipitate was collected by filtration, washed with water several times, and air-dried overnight. The solid (69.5 mg) was purified on alumina column with dichloromethane and then dichloromethane/MeOH (gradient 99.9:0.1) to give 52.2 mg (0.024 mmol, 88%) of **3**. Finally, this compound was recrystallized by diffusion of diethyl ether into a solution of acetonitrile/diethyl ether to afford 48.3 mg (81%) of $DPPIr_2$ as orange crystals. NMR and ESI-MS are in quantitative agreement with previously reported values.[42] ^{1}H NMR (400 MHz, CD_3CN), δ (ppm): 8.54 (t, *J* = 7.3 Hz, 4H), 8.25 (dd, ^3J = 8.5 Hz, ^4J = 2.0 Hz, 2H), 8.14 (td, ^3J = 7.9 Hz, ^4J = 1.6 Hz, 2H), 8.03−8.11 (m, 6H), 8.00 (d, *J* = 5.4 Hz, 2H), 7.78−7.90 (m, 12H), 7.72 (d, *J* = 5.9 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 4H), 7.61 (d, *J* = 5.9 Hz, 2H), 7.49−7.55 (m, 2H), 7.01−7.11 (m, 8H), 6.96 (td, ^3J = 7.4 Hz, ^4J = 1.2 Hz, 2H), 6.93 (td, ^3J = 7.5 Hz, ^4J = 1.3 Hz, 2H), 6.32 (dd, ^3J = 7.6 Hz, ^4J = 0.8 Hz, 2H), 6.27 (dd, ^3J = 7.7 Hz, ^4J = 0.8 Hz, 2H), 3.65−3.79 (m, 4H), 1.24−1.36 (m, 2H), 0.98−1.22 (m, 16H), 0.77 (t, *J* = 6.9 Hz, 6H), 0.68 (t, *J* = 7.4 Hz, 6H). ESI-MS (dichloromethane/acetonitrile) positive mode of analysis: 2015.4 ([M-PF_6], 100), 935.2 ([M-2PF_6], 30). Anal. Calcd for $C_{102}H_{88}F_{12}Ir_2N_{10}O_2P_2$: C, 56.71; H, 4.11; N, 6.48; Found: C, 56.44; H, 3.85; N, 6.34%.

$[DPPIr](PF_6)$ (2). This complex was prepared in a similar manner to the dinuclear complex using **1** (49.6 mg, 0.057 mmol) in dichloromethane (10 mL) and MeOH (2 mL) and $[Ir(ppy)_2Cl]_2$ (31.0 mg, 0.0285 mmol) affording 28.8 mg (0.019 mmol, 69%) of **2**. ^{1}H NMR (400 MHz, CD_2Cl_2), δ (ppm): 9.39 (dd, ^3J = 26.5 Hz, ^4J = 8.3 Hz, 2H), 8.83 (d, *J* = 1.8 Hz, 1H), 8.67 (d, *J* = 4.3 Hz, 1H), 8.46 (t, *J* = 8.1 Hz, 2H), 8.33 (dd, ^3J = 8.7 Hz, ^4J = 2.0 Hz, 1H), 8.24 (td, ^3J = 8.0 Hz, ^4J = 2.0 Hz, 1H), 8.07 (d, *J* = 2.0 Hz, 1H), 7.93−8.02 (m, 4H), 7.69−7.87 (m, 11H), 7.56−7.65 (m, 3H), 7.49−7.53 (m, 1H), 7.42−7.48 (m, 1H), 7.30−7.37 (m, 1H), 6.90−7.16 (m, 6H), 6.27−6.38 (m, 2H), 3.67−3.82 (m, 4H), 1.19−1.35 (m, 2H), 1.00−1.18 (m, 16H), 0.80 (q, *J* = 6.9 Hz, 6H), 0.71 (q, *J* = 7.3 Hz, 6H). ESI-MS (dichloromethane/acetonitrile) positive mode of analysis: 1369.4 ([M-PF_6], 100). Anal.

Calcd for $C_{80}H_{72}F_6IrN_8O_2P$: C, 63.44; H, 4.79; N, 7.40; Found: C, 63.22; H, 4.56; N, 7.23%.

DPPPtCl$_2$. This complex was prepared from **1** (49.6 mg, 1 equiv, 0.057 mmol) in tetrahydrofuran (THF) (5 mL) and $Pt(DMSO)_2Cl_2$ (24.8 mg, 0.059 mmol). The reaction mixture was heated to 60 °C overnight. During the course of the reaction a deep-red precipitate formed, which was recovered by centrifugation and washed with cold THF and diethyl ether. The precipitate was purified on an alumina column with dichloromethane then dichloromethane/MeOH (gradient 99.9:0.1) to give 45.1 mg (0.056 mmol, 86%) of DPPPtCl$_2$. ^{1}H NMR (400 MHz, CD_2Cl_2), δ (ppm): 9.34 (s, 1H), 9.18 (d, J = 5.6 Hz, 1H), 8.60 (s, 1H), 8.43 (d, J = 1.9 Hz, 1H), 8.41 (d, J = 2.0 Hz, 1H), 8.18−8.31 (m, 3H), 8.14 (t, J = 6.9 Hz, 2H), 7.76 (dd, ^3J = 8.3 Hz, ^4J = 1.9 Hz, 1H), 7.52−7.72 (m, 5H), 7.46−7.52 (m, 2H), 7.36−7.46 (m, 3H), 7.16 (dd, ^3J = 7.4 Hz, ^4J = 5.4 Hz, 1H), 3.52−3.78 (m, 4H), 1.18−1.38 (m, 2H), 0.95−1−17 (m, 16H), 0.74−0.84 (m, 6H), 0.60−0.72 (m, 6H). ESI-MS (dichloromethane/acetonitrile) positive mode of analysis: 1134.2 ([M + H], 100), 1099.2 ([M-Cl], 25). Anal. Calcd for $C_{58}H_{56}Cl_2N_6O_2Pt$: C, 61.37; H, 4.97; N, 7.40; Found: C, 61.19; H, 4.74; N, 7.23%.

DPPPt (4). This complex was prepared from DPPPtCl$_2$ (50 mg, 0.044 mmol) dissolved in DMF (10 mL), tetrahydrofyran (10 mL), triethylamine (3 mL) and tolylacetylene (26.0 mg, 0.220 mmol). The solution was degassed by bubbling with argon for 30 min, and CuI (10 mg) was added. The reaction mixture was stirred overnight under argon, then the solution was evaporated to dryness. The residue was dissolved in dichloromethane and washed with water. The organic phase was dried over anhydrous Na_2SO_4 and evaporated to dryness. The residue was purified by column chromatography on alumina using dichloromethane and dichloromethane/MeOH (gradient 99.9:0.1) as the mobile phase to give 49.5 mg (0.038 mmol, 87%) of **4**. ^{1}H NMR (400 MHz, CD_2Cl_2), δ (ppm): 9.49 (d, J = 1.2 Hz, 1H), 9.16 (d, J = 5.4 Hz, 1H), 8.59 (d, J = 1.3 Hz, 1H), 8.36−8.47 (m, 2H), 8.32 (d, J = 7.6 Hz, 1H), 8.26 (dd, ^3J = 8.1 Hz, ^4J = 1.5 Hz, 1H), 8.12 (t, J = 6.7 Hz, 2H), 8.06 (t, J = 7.6 Hz, 1H), 7.75 (dd, ^3J = 8.2 Hz, ^4J = 2.1 Hz, 1H), 7.52−7.71 (m, 7H), 7.39−7.46 (m, 4H), 7.28−7.39 (m, 5H), 7.10−7.22 (m, 3H), 3.57−3.84 (s, 4H), 2.54 (s, 3H), 2.40 (s, 3H), 1.20−1.34 (m, 2H), 0.93−1.19 (m, 16H), 0.74−0.86 (m, 6H), 0.58−0.73 (m, 6H). ESI-MS (dichloromethane/acetonitrile) positive mode of analysis: 1295.4 ([M + H], 100). Anal. Calcd for $C_{76}H_{70}N_6O_2Pt$: C, 70.52; H, 5.45; N, 6.49; Found: C, 70.39; H, 5.27; N, 6.14%.

[DPPPtIr](PF$_6$) (5). To a solution of **4** (28.3 mg, 0.0219 mmol) in dichloromethane (5 mL) was added MeOH (1 mL). The reaction mixture was heated to 60 °C to completely dissolve the starting material. Then the $[Ir(ppy)_2Cl]_2$ dimer in dichloromethane/MeOH (14.1 mg, 0.0131 mmol) was added, and the solution was heated at 60 °C for 15 h. The mixture was cooled to RT and concentrated under reduced pressure. The residue was dissolved in a minimum of DMF (2.5 mL), and this solution was added slowly to a stirred solution of KPF_6 (50 equiv, 201 mg) in water (4 mL). A red precipitate formed and was collected by filtration, washed with water several times, and air-dried overnight. The residue was purified on an alumina column with dichloromethane and dichloromethane/MeOH (gradient 99.9:0.1 to 99.7:0.3) to give 18.7 mg (0.0096 mmol, 44%) of **5**. ^{1}H NMR (400 MHz, CD_2Cl_2), δ (ppm): 9.80 (s, 1H), 9.51 (d, J = 5.3 Hz, 1H), 8.54 (t, J = 7.7 Hz, 2H), 8.00−8.33 (m, 8H), 7.97 (t, J = 8.5 Hz, 2H), 7.72−7.85 (m, 6H), 7.61−7.71 (m, 3H), 7.38−7.57 (m, 9H), 7.29−7.36 (m, 2H), 7.18−7.25 (m, 2H), 6.87−7.16 (m, 8H), 6.23−6.37 (m, 2H), 3.55−3.79 (m, 4H), 2.44 (s, 3H), 2.36 (s, 3H), 1.23−1.36 (m, 2H), 0.96−1−21 (m, 16H), 0.74−0.84 (m, 6H), 0.62−0.73 (m, 6H). ESI-MS (dichloromethane/acetonitrile) positive mode of analysis: 1939.4 ([M-PF$_6$], 100). Anal. Calcd for $C_{98}H_{86}F_6IrN_8O_2PPt$: C, 60.67; H, 4.47; N, 5.78; Found: C, 60.45; H, 4.36; N, 5.56%.

Steady-State Spectroscopy. Compounds were stored in an inert atmosphere glovebox (MBraun). Spectroscopic samples were prepared in an inert atmosphere glovebox (MBraun) using spectrophotometric grade acetonitrile, which was previously degassed with a minimum of five freeze−pump−thaw cycles, in 1 cm^2 anaerobic cells unless otherwise noted. Complexes **1** and **4** are only sparingly soluble in acetonitrile; therefore, solutions were filtered through a 0.45 μm filter before measuring. Absorption spectra were acquired using an Agilent 8453 diode array spectrophotometer. Steady-state emission spectra were collected with a FS920 fluorometer (Edinburgh Instruments) equipped with a 450 W Xe arc lamp as the excitation source. The emission signal was detected with a Peltier-cooled, red-sensitive PMT (R2658P Hamamatsu). Low-temperature spectra were collected using an Optistat-DN optical cryostat and ITC-503 temperature controller (Oxford Instruments). Measurements were taken at 77.2 K in a 9:2 mixture of butyronitrile and propionitrile. All low-temperature samples were bubble degassed with nitrogen for 20 min prior to cooling and were allowed to equilibrate for 30 min at 77 K before each measurement.

The quantum yields for **2**−**5** were measured with the FS920 fluorometer relative to the $[Ru(bpy)_3](PF_6)_2$ standard in aerated acetonitrile (Φ = 0.018).[66] Optically dilute (OD = 0.1−0.2) solutions were excited into the lowest energy absorption feature (λ_{ex} = 500 nm). The absolute quantum yield for complex **1** was recorded with a Hamamatsu absolute quantum yield spectrometer (C11347). A saturated, filtered solution in deaerated acetonitrile (OD < 0.1) was excited at 500 nm, and reported value is the average of six measurements.

Time-Resolved Spectroscopy. Time-resolved fluorescence experiments were accomplished using a time-correlated single-photon counting (TCSPC) spectrometer that has been described previously.[67] For all measurements, the Chameleon laser was tuned to 1000 nm, pulse picked to a 4 MHz repetition rate (Coherent 9200 Pulse Picker), and frequency doubled (APE-GmbH SHG Unit) to yield 500 nm excitation. The long-lived (ns) kinetic traces were fit with single exponential functions using IGOR Pro.

Transient absorption data were collected with an LP920 laser flash photolysis system (Edinburgh Instruments) using the Vibrant 355 LD-UVM Nd:YAG/OPO system (OPOTEK) as the excitation source (λ_{ex} = 500 nm, ~2.0 mJ/pulse). Data acquisition was controlled by the LP900 software program (Edinburgh Instrument). Samples were prepared with an optical density of 0.3−0.5 at the excitation wavelength. Kinetic traces were collected with a PMT (R928 Hamamatsu), and transient absorption spectra were collected with an iStar ICCD camera (Andor Technology). Kinetic traces were fit with single exponential functions using IGOR Pro.

Calculations. Calculations were performed using the Gaussian 09 software package[68] through the Ohio Supercomputer Center and North Carolina State University High Performance Computing Center. Geometry optimizations were done using the B3LYP functional and the LANL2DZ[69] basis set on Ir and Pt atoms and the 6-31G(d)[70] basis set on all other atoms. For all structures the aliphatic chains on the DPP ligand were replaced with methyl groups to simplify the calculation. The polarizable continuum model (PCM) was used to simulate the effect of the acetonitrile solvent environment.[71] Frequency calculations were performed on the optimized geometries to ensure the calculated geometries corresponded to global minima. No imaginary frequencies were found for any optimized structure. Highest occupied molecular orbitals (HOMOs) and LUMOs for each structure were visualized using GaussView5.[72]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra along with low-temperature and room temperature emission decay traces, orbital visualizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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