Excitation energy-dependent photocurrent switching in a single-molecule photodiode

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Abstract

The direction of electron flow in molecular optoelectronic devices is dictated by charge transfer between a molecular excited state and an underlying conductor or semiconductor. For those devices, controlling the direction and reversibility of electron flow is a major challenge. We describe here a novel, single-molecule photodiode. It is based on an internally conjugated, bi-chromophoric dyad with chemically linked (porphyrinato)zinc(II) and bis(terpyridyl)ruthenium(II) groups. On nanocrystalline, degenerately doped indium tin oxide electrodes, the dyad exhibits distinct frequency-dependent, charge-transfer characters. Variations in the light source between red (~ 1.9 eV) and blue (~ 2.7 eV) light excitation for the integrated photodiode result in switching of photocurrents between cathodic and anodic. The origin of the excitation frequency-dependent photocurrents lies in the electronic structure of the chromophore excited states, as shown by the results of theoretical calculations, laser flash photolysis and steady-state spectrophotometric measurements.

Significance

In optoelectronic devices based on the properties of molecular excited states, a major challenge exists in controlling wavelength-dependent properties, because of the rapid interconversion between excited states. In photoelectrochemical cells, based on dye-sensitized photoelectrodes, surface-functionalization plays a significant role in directing the absorption and conversion of incident photons. We demonstrate here that the direction of photo-generated charge flow in an oxide-based photoelectrode can be controlled by varying the excited-state transitions in a surface-bound highly conjugated supramolecular chromophore with important implications for photoelectrode design in molecular devices. This approach, with a well-established correlation between conjugated chromophores and oxide electrodes, can serve as an effective platform for further development of solar-energy conversion devices.

Introduction

Devices based on molecular electronics mimic traditional macroscopic semiconductor devices but provide unprecedented advantages in scalable size, synthetic flexibility and controllable electronic properties (1, 2). With those devices, electrical and electronic processes can be modified by varying functional electrode elements and integrating individual molecular components that respond to external stimuli, such as electrochemical redox potentials, optical excitation and magnetic fields (3-7). Photo-responsive molecular diodes have been used in dye-sensitized photoelectrodes to generate electron-hole pairs for catalytic and optoelectronic applications (8-14). They convert solar energy into electrical signals and chemical energy by transfer of photogenerated electrons following optical excitation. For those devices, controlling the direction of the electron flow is a challenge, even for multi-chromophoric systems, because of competition from excited-state relaxations and back electron transfer (15-17). Creating a local basis for controlling the direction of electron flow requires the formation of chromophoric excited states with aligned energetics for rapid charge injection into the electrode substrates. Under a certain range of applied bias, a localized interfacial charge-separation state can be used to produce sustainable external photocurrents.

Here, we describe a dye-sensitized photoelectrode that generates photocurrents with direction controllable by varying the frequency of the excitation photons. The photoelectrode was fabricated with a degenerately doped, nanocrystalline indium tin oxide electrode (*nano*ITO) (18) which was sensitized by a highly conjugated, supramolecular chromophore. The chromophore (abbreviated as $(PhZnRu)^{2+}$) in Fig. 1A and a structural analog (abbreviated as $(RuZn)^{2+}$) in Fig. 1B are ethyne-bridged (porphyrinato)zinc(II) and bis(terpyridyl)ruthenium(II) complexes with carboxylic or phosphonic acid groups for surface-binding to *nano*ITO electrodes. This connectivity aligns the bis(terpyridyl)ruthenium(II) and (porphyrinato)zinc(II) transition dipoles in a head-to-tail arrangement, enforcing extensive excited-state electronic communication between these units, and driving significant charge-transfer (CT) character in the chromophore's three low energy singlet excited state manifolds. (19-24) The two chromophores on *nano*ITO exhibits frequency-dependent, excited-state charge-transfer characters at their excited states. Alternation of the excitation source between red and blue light for the integrated photodiode with $(PhZnRu)^{2+}$ on *nano*ITO results in switching of photocurrents between cathodic and anodic. Based on the results from theoretical calculations, transient absorption and steady-state spectrophotometric measurements, the excitation-frequency-dependent photocurrents originate from the changes in the electron density distributions within the chromophore excited states.

Results and Discussion

Molecular Design and Electronic Spectroscopy. Characterization data for $(PhZnRu)^{2+}$ and $(RuZn)^{2+}$ are shown in Figs. S1-S6. The electronic absorption spectra recorded for $(PhZnRu)^{2+}$ and $(RuZn)^{2+}$ in Fig.1 differ markedly from those characteristics of individual (porphyrinato)zinc(II) (abbreviated as Zn)) and bis(terpyridyl)ruthenium(II) (abbreviated as Ru^{2+}) complexes. In $(PhZnRu)^{2+}$ and $(RuZn)^{2+}$, extensive mixing of PZn B- and Q-electronic states with ruthenium terpyridyl metal-ligand charge transfer (MLCT) states gives rise to supramolecular chromophores that manifest high oscillator strength absorptive manifolds that provide an unusual degree of spectral coverage of the 250-750 nm wavelength domain (19-24). Note that $(PhZnRu)^{2+}$ is anchored to *nano*ITO photoelectrodes through its PZn-appended 5'(4-carboxypheneyl ethynyl) group (Fig. 1A), while $(RuZn)^{2+}$ is similarly attached via it 4"-terpyridyl-phosphonic acid group (Fig. 1B). Surface loading of these assemblies on *nano*ITO photoelectrodes was determined to be ~28-31 nmol/cm^2 from electronic absorption measurements in Table S1.

Figure 2 describes the respective natural transition orbitals (NTOs) for $(PhZnRu)^{2+}$ and $(RuZn)^{2+}$ determined from linear-response, time-dependent density functional theory (TDDFT) calculations (24-27) as a function of excitation wavelength. These NTOs were calculated by taking linear combinations of molecular orbitals according to their contributions to individual excited states produced in these supramolecular chromophores upon red and blue light excitation. For these excited states that feature substantial CT character, orbital isosurfaces (NTO(e^-) and NTO(h^+)) display the location and spatial extent of electron and hole delocalization. Note the differences in the natures of these NTOs determined for $(PhZnRu)^{2+}$ as a function of excitation wavelength: red excitation (~ 1.9 eV) gives rise to an excited state described by PZn-to-Ru CT, while blue excitation (~ 2.7 eV) generates an excited-state that features Ru-to-PZn charge-transfer character (Fig. 2A). Red light photoexcitation of $(PhZnRu)^{2+}$ creates a long-lived triplet excited state [$^3(PhZnRu)_r{}^{*2+}$] with a lifetime (τ) of ~ 6.7 μs (Fig. S7). The red-light excited state bears resemblance to semiconductor p–n junctions, with electron density delocalized on the ethynyl-terpyridyl ligand of Ru^{2+}, and hole density on the phenyl-ethynyl-porphyrin fragment of PhZn (Fig. 2A). The NTO(e^-) and NTO(h^+) of $(PhZnRu)_r{}^{*2+}$ resemble the LUMO and HOMO of the $(PhZnRu)^{2+}$ ground state determined from density functional theory (DFT) calculations (Fig. S8).

The red-light triggered electron transfer sequence for $(PhZnRu)^{2+}$ anchored on *nano*ITO is illustrated in Fig. 3A. Hole injection into *nano*ITO under a mild applied bias from $(PhZnRu)_r{}^{*2+}$ is facilitated by the spatial distribution of its NTO(h^+), producing the reduced chromophore ($(PhZnRu)^+$). Similarly, as illustrated in Fig. 2B, red-light excitation of $(RuZn)^{2+}$ results in an excited state described by NTO(e^-) and NTO(h^+) that are delocalized respectively over the Ru^{2+} ethynyl-terpyridyl ligand and the porphyrin framework. In contrast to the case for $(PhZnRu)^{2+}$, under a mild applied bias, the $(RuZn)^{2+}$ red-light excited state injects an electron into *nano*ITO (see the spatial distribution of its NTO(e^-), Fig. 2B), forming the oxidized chromophore $(RuZn)^{3+}$, as illustrated in Fig. 3C.

As shown in Fig. 2A, the calculated NTO(e^-) for the blue-light (~ 2.7 eV) excited state, $(PhZnRu)_b{}^{*2+}$, features an isosurface on the porphyrin and the bridging terpyridyl ligand. The NTO(h^+) isosurface of $(PhZnRu)_b{}^{*2+}$ is dominated by the porphyrin unit of PhZn. The analysis reveals that blue-light excitation of $(PhZnRu)^{2+}$ does not give rise to an excited state with substantial CT character. These results are in contrast to the NTOs of the blue-light excited state of $(RuZn)^{2+}$ (Fig. 2B). For $(RuZn)_b{}^{*2+}$, the electron density is largely delocalized on the Ru^{2+} ethynyl-terpyridyl ligand, while the hole density is confined to the Zn ethynyl-porphyrin fragment, as shown by the NTO(e^-) and NTO(h^+) in Fig. 2B. Under mild applied bias on *nano*ITO, electron injection occurs from the blue-light excited states of $(PhZnRu)_b{}^{*2+}$ and $(RuZn)_b{}^{*2+}$. The NTO(e^-) electron density spatial distributions for both these supermolecules are poised for electron injection at the *nano*ITO surface, resulting in production of the one-electron oxidized chromophores, $(PhZnRu)^{3+}$ and $(RuZn)^{3+}$. The electron transfer sequences are illustrated in Fig. 3B for *nano*ITO|-$(PhZnRu)_b{}^{*2+}$ and in Fig. 3D for *nano*ITO|-$(RuZn)_b{}^{*2+}$.

Simulated UV-Vis absorption spectra from linear-response TDDFT calculation for $(PhZnRu)^{2+}$ and $(RuZn)^{2+}$ are given in Figs. S9 and S10. As shown in both spectra, the low-energy peaks with intramolecular charge-transfer characters are red-shifted compared to the experimental spectra. It can be attributed to the fact that solvent was not included in the TDDFT calculations, which precludes observation of the expected solvatochromic shifts. However, the qualitative trends are quite similar between the simulated and experimental spectra. The assignments for the peaks and NTOs are relatively straightforward, with three dominant broadened peaks appearing in both simulated spectra. For $(RuZn)^{2+}$, there are two excited states with comparable oscillator strengths (ES55 and ES66 in Fig. S10). In this case, the lower-energy excited state, ES55, is assigned to the "blue" ~2.7 eV excitation because, as shown by the blue-shaded region in Fig. 1B, the excitation energy is more closely aligned with the shoulder, rather than the maximum, of the peak. For completeness, the NTOs for other excitations (ES19 for $(PhZnRu)^{2+}$, ES29 and ES55 for $(RuZn)^{2+}$) are also displayed in Figs. S9 and S10.

Photocurrent Variation with the Excitation Energy. TDDFT computations for the chromophore excited state NTOs provide a framework for controlling the direction of electron flow at $(PhZnRu)^{2+}$-functionalized photoelectrodes. To explore the point in experimental details, the $(PhZnRu)^{2+}$-functionalized *nano*ITO electrode was irradiated by red light (λ_{max}: 650 nm, 20 nm FWHM, ~ 10 mW/cm^2) or blue light (λ_{max}: 455 nm, 20 nm FWHM, ~ 7.0 mW/cm^2) with a solid-state light source (Lumencor Inc., photon flux: 38 nmol/cm^2/s). By alternating between red- and blue-light irradiation, the photoelectrode *nano*ITO|-$(PhZnRu)^{2+}$ under a bias at 0.20 V vs NHE produces persistent photocurrents that switch between cathodic and anodic in the redox buffer containing sacrificial electron donor (ascorbic acid, 0.77 mM) (28) and acceptor (4,4'-dipyridyl disulfide, 0.77 mM) (29), as shown in Fig. 4A. These photocurrent responses were reproduced when *nano*ITO|-$(PhZnRu)^{2+}$ was irradiated by only red (Fig. 4B) or blue light (Fig. 4C). With red light, the excited state $(PhZnRu)_r{}^{*2+}$ injects the hole into *nano*ITO to give cathodic photocurrents. With blue light, *nano*ITO|-$(PhZnRu)^{2+}$ produces anodic photocurrents through electron injection by $(PhZnRu)_b{}^{*2+}$. As illustrated in Fig. 3A,B, injection leads to formation of $(PhZnRu)^{+}$ by red-light excitation or $(PhZnRu)^{3+}$ by blue-light excitation. With the added redox buffer, persistent cathodic or anodic photocurrents result from the reduction of 4,4'-dipyridyl disulfide by $(PhZnRu)^{+}$ or the oxidation of ascorbic acid by $(PhZnRu)^{3+}$, respectively, in the redox buffer. The energy diagrams in Fig. S11A,B give the directions of the photogenerated electron transfer processes for *nano*ITO|-$(PhZnRu)^{2+}$ upon red and blue excitation.

The photocurrent switching behavior is absent for *nano*ITO|-$(RuZn)^{2+}$ under the same conditions, as shown in Fig. 4D-F. Either red- or blue-light irradiation results in anodic photocurrents and photo-oxidation of ascorbic acid in the redox buffer. In contrast to the data acquired for *nano*ITO|-$(PhZnRu)^{2+}$, electron injection at the photoelectrode is driven by both the red- ($(RuZn)_r{}^{*2+}$) and blue-light ($(RuZn)_b{}^{*2+}$) excitation of this chromophore (Fig. 3C,D). The electron transfer steps are illustrated in the energy diagrams in Fig. S11C,D. The magnitudes of the photocurrents from *nano*ITO|-$(RuZn)^{2+}$ under blue-light irradiation are ~ 1.4 times higher than the photocurrents obtained by red-light irradiation. The similar light-absorption efficiencies for red and blue excitation (Table S1) and the common photon flux (38 nmol/cm^2/s), suggest no significant differences in the number of absorbed red or blue photons; hence, variations in the observed photocurrents may result from the differences in charge injection efficiencies, interfacial charge recombination kinetics, or other factors.

Excited-State Electron Transfer. Pump-probe transient absorption data for $(RuZn)^{2+}$ and $(PhZnRu)^{2+}$ adsorbed on nanoITO electrodes show ultrafast dynamics that are absent for these chromophores in solution, such as what would be expected for light-driven charge injection. The ultrafast transient absorption (TA) spectra for the samples without the sacrificial electron donors/acceptors are shown in Fig. S12. The time-resolved traces in the insets were fitted to the biphasic Kohlrausch-Williams-Watts (KWW) function (see Materials and Methods) (11). The fitting parameters are listed in Table S2. From the TA spectra in Fig. S12A, decay of the red-light excited state ($(PhZnRu)_r{}^{*2+}$) on a 1.28 ps timescale is consistent with hole injection into nanoITO followed by rapid charge recombination. Hole injection occurs due to the high hole density on the phenyl-ethynyl-porphyrin fragment of PhZn at $(PhZnRu)_r{}^{*2+}$. Under an applied bias at 0.45 V vs NHE, a fraction of injected holes are driven to the back contact, leaving the rest at the interface recombining with the electrons at $(PhZnRu)^{+}$. The nanosecond TA in Fig. S13 illustrates the appearance and decay of the injection product, the reduced chromophore $(PhZnRu)^+$ (see the spectroelectrochemical data in Fig. S14A). The decay of $(PhZnRu)^+$ occurs on the microsecond timescale due to the interfacial charge recombination with the holes at *nano*ITO surface traps (11). Under blue light excitation, ultrafast injection dynamics likely occur within the time-resolution (250 fs) of our instrument, as evidenced by (i) the comparatively weak TA spectra relative to those after red-light excitation; and (ii) the spectra observed at the earliest time delays already resemble that of the oxidized state (Fig. S14B). The nanosecond TA in Fig. S15 shows the absorptive features of $(PhZnRu)^{3+}$ (see the spectroelectrochemical data in Fig. S14B) which decays in ~ 5 μs due to charge recombination with *nano*ITO(e^-). The positive applied bias helps to drive the injected electrons to the back contact and slowing down back electron transfer to $(PhZnRu)^{3+}$. The electron transfer steps are illustrated schematically in Fig. 3A,B.

Red- or blue-light excitations of *nano*ITO|-$(RuZn)^{2+}$ lead to formation of the excited-states ($(RuZn)_r{}^{*2+}$ or $(RuZn)_b{}^{*2+}$) with TA features shown in Figs. S12C,D. Biphasic KWW fitting of the time-resolved TA data in the insets gives timescales of ~ 1.70 – 1.79 ps for electron injection into *nano*ITO. The nanosecond TA spectra in Figs. S16 and S17 for red- and blue-light excitation of *nano*ITO|-$(RuZn)^{2+}$ show similar absorptive changes, consistent with the appearance of the oxidized chromophore ($(RuZn)^{3+}$) with the spectroelectrochemical data in Fig. S14D. The decay of $(RuZn)^{3+}$ through charge recombination with *nano*ITO(e^-) in both cases is complete within ~ 10 μs. For *nano*ITO|-$(RuZn)^{2+}$ under red or blue excitation, interfacial charge recombination between nanoITO(e^-) and $(RuZn)^{3+}$ is decelerated under the positive applied bias. The electron transfer sequences are illustrated in Fig. 3C,D.

Fig. 5 illustrates how surface coverages (Γ) of the oxidized or reduced chromophores vary as the applied bias (ΔE) is modulated under red- or blue-light irradiation. The surface coverage changes (ΔΓ) were evaluated by spectroelectrochemical measurements (30) for the chromophores on *nano*ITO (see details in Materials and Methods, and Fig. S18). As shown by the blue trace in Fig. 5A, blue-light irradiation of *nano*ITO|-$(PhZnRu)^{2+}$ leads to rapid growth in $\Delta\Gamma((PhZnRu)^{3+})$ as ΔE is increased. The growth in $\Delta\Gamma((PhZnRu)^{3+})$ slows as the bias is adjusted positively past the maximum point of $\Delta\Gamma((PhZnRu)^{3+})/\Delta E$ at ~ 0.17 V vs NHE. Compared to electrochemical oxidation of $(PhZnRu)^{2+}$ in the dark (gray line in Fig. 5A), the blue-light induced photo-oxidation of $(PhZnRu)^{2+}$ occurs over a much lower potential range. Since the applied bias dictates the Fermi level of the *nano*ITO electrode (31), a more positive bias lowers the thermodynamic barrier for electron injection by the excited states.

As discussed above, the red-light excited state, $(PhZnRu)_r{}^{*2+}$, injects a hole into *nano*ITO to give the reduced chromophore, $(PhZnRu)^+$, with the yield of formation controlled by the injection step. Fig. 5B illustrates the decrease in $\Gamma((PhZnRu)^+)$ as the bias is shifted positively. Increasing the flat band potential of *nano*ITO positively leads to less favored hole injection by $(PhZnRu)_r{}^{*2+}$ and rapidly decreased $\Delta\Gamma((PhZnRu)^+)/\Delta E$ in Fig. 5B. For the photoelectrode *nano*ITO|-$(RuZn)^{2+}$ under blue- or red-light irradiation, the injected electrons at *nano*ITO(e^-) are transported to the external circuit by the positive applied bias, leaving the holes at $(RuZn)^{3+}$. In Fig. 5C,D, $\Delta\Gamma((RuZn)^{3+})$ increases rapidly with the increase of the bias; note the respective ΔΓ/ΔE maxima at 0.14 V and 0.17 V vs NHE for the blue- and red-light excited *nano*ITO|-$(RuZn)^{2+}$, respectively. Past those biases, ΔΓ/ΔE decreases exponentially. As shown by the gray lines in Fig. 5C,D, the unirradiated photoelectrode forms $(RuZn)^{3+}$, but in much higher positive potential range. The Fermi level of the degenerately doped nanoITO electrode is determined by the applied bias, which allows for facile control of the injection dynamics for *nano*ITO|-$(RuZn)^{2+}$ and *nano*ITO|-$(RuZn)^{2+}$ under different excitation energies. It can be expected that the dependence of injection dynamics on excitation energies is less pronounced when the nanoITO electrode is replaced by rectifying oxides, e.g., p-type NiO or n-type TiO_2, as illustrated by the proposed energy (redox) level diagrams in Fig. S19.

Conclusions

The results described here demonstrate remarkable changes in charge-transfer behaviors for the bichromophoric dyad, (PhZnRu)$^{2+}$, on nanocrystalline ITO electrode upon excitation at different photon energies. Under red-light excitation, hole transfer from the lower energy (PhZnRu)$_{r}$*$^{2+}$ state to the electrode occurs, generating cathodic photocurrents in a redox buffer containing a sacrificial electron acceptor. In contrast, with blue light excitation, (PhZnRu)$_{b}$*$^{2+}$ injects an electron into the conduction band of *nano*ITO to give anodic photocurrents which were sustained with the presence of a diffusional electron donor in solution. The variation in behaviors, which is remarkable from the photophysical point of view, is microscopically derived from the different internal charge-transfer characteristics of the excited states. The excitation-energy dependent processes that drive either hole or electron injection at *nano*ITO are important from a device perspective. They establish a basis for wavelength-dependent, single-molecule photoelectrodes whose outputs depend on the excitation photon energy. As an approach for applications in photodiodes, the (PhZnRu)$^{2+}$-functionalized *nano*ITO electrode contrasts benchmarks in this field that rely upon significant variations in molecular or material properties for photocurrent control in optoelectronic junctions.

Materials and Methods

Synthesis of (PhZnRu)$^{2+}$. The synthetic scheme is shown in Fig. S20. The precursors, ZnE and (RuBr)$(PF_6)_2$ were synthesized by using the procedures published earlier (20). In a 100 mL Schlenk tube ZnE (0.154 mmol) and (RuBr)$(PF_6)_2$ (0.123 mmol) were added with a stir bar. Trisdibenzylideneacetone dipalladium(0) (16.4 mol) and triphenylarsine (0.164 mmol) were then added. A solvent mixture of dry THF (18 mL), CH_3CN (36 mL) and Et_3N (8 mL) was thoroughly degassed by argon and added to the Schlenk tube. The reaction mixture was stirred under argon at 55 °C for 16 h. The reaction mixture was cooled to room temperature and the solvent was evaporated. The residue was purified by column chromatography on silica gel eluted with a mixed solvent of $CH_3CN:H_2O:KNO_3$ (aq.) = 90:9:1. The green-brown band from the column was collected and solvent was evaporated. The residual dark brown solid was dissolved in a minimum volume of CH_3CN, following by addition of excess ammonium hexafluorophosphate and H_2O. Dark brown precipitate of (EZnRu)$(PF_6)_2$ (106 mg, 56% yield based on (RuBr)$(PF_6)_2$) was collected by filtration.

In a 100 mL Schlenk tube (EZnRu)$(PF_6)_2$ (0.059 mmol) and 4-iodocarboxylic acid (0.118 mmol) were placed with a stir bar. Trisdibenzylideneacetone dipalladium(0) (16.4 μmol) and triphenylarsine (0.164 mmol) were added. A solvent mixture of dry THF (18 mL), CH_3CN (36 mL) and Et_3N (8 mL) was thoroughly degassed by argon and added to a Schlenk tube. The reaction mixture was stirred under argon at 50 °C for 2 h. The reaction mixture was cooled to room temperature and the solvent was evaporated. The residue was purified by column chromatography on silica gel eluted with a mixed solvent of $CH_3CN:H_2O:KNO_3$ (aq.) = 90:9:1. The major green-brown band was collected, and solvent was evaporated. The residual dark brown solid was dissolved in minimum volume of CH_3CN, followed by addition of excess ammonium hexafluorophosphate and H_2O. A dark brown precipitate of (PhZnRu)$(PF_6)_2$ (58 mg, 60% yield) was collected by filtration.

^{1}H NMR in Fig. S1 (500 MHz, DMSO-d_6) δ 9.99 (d, J = 4.5 Hz, 2H), 9.84 (s, 2H), 9.67 (d, J = 4.5 Hz, 2H), 9.21 (d, J = 8.1 Hz, 2H), 9.15 (d, J = 8.2 Hz, 2H), 8.88 (d, J = 8.2 Hz, 2H), 8.83 (d, J = 4.5 Hz, 1H), 8.74 (d, J = 4.5 Hz, 1H), 8.60 (t, J = 8.2 Hz, 1H), 8.29 – 8.13 (m, 5H), 8.06 (td, J = 7.8, 1.5 Hz, 2H), 7.83 (t, J = 8.5 Hz, 2H), 7.75 – 7.67 (m, 3H), 7.66 – 7.56 (m, 2H), 7.53 (dd, J = 5.6, 1.5 Hz, 2H), 7.40 – 7.29 (m, 4H), 7.22 (d, J = 8.7 Hz, 4H), 3.97 (t, J = 7.3 Hz, 8H), 0.86 (t, J = 7.2 Hz, 8H), 0.30 (s, 36H). ^{13}C NMR in Fig. S2 (126 MHz, DMSO-d_6) δ 166.94, 159.33, 157.80, 157.78, 155.05, 154.74, 152.49, 152.19, 151.29, 150.76, 150.59, 150.36, 138.26, 138.16, 136.16, 133.45, 132.33, 132.13, 131.56, 130.92, 130.51, 130.32, 129.93, 129.54, 128.00, 127.82, 127.65, 125.34, 124.99, 124.64, 124.12, 119.61, 116.44, 105.17, 101.18, 99.24, 96.68, 95.91, 95.27, 93.54, 65.49, 41.43, 28.92, 28.88. Electrospray ionization mass spectrometry (ESI-MS) in Fig. S3: m/z = 830.27872 (z = 2).

Synthesis of $(RuZn)^{2+}$. The synthetic scheme is shown in Fig. S21. The precursors, ZnE' (21), TerpyBr (22), ZnTerpy (20), $ZnRuCl_3$ (32), $terpyPO_3H_2$ (32), were prepared based on the previously reported procedures (20-22, 32). $ZnRuCl_3$ (138.9 mg, 0.1 mmol), $terpyPO_3H_2$ (31.3 mg, 0.1 mmol), triethylamine (4 mL) and ethanol (5 mL) were added in N-methylpyrrolidone (30 mL). NH_4PF_6 (32.6 mg, 0.2 mmol) was added after the solution mixture was stirred at 120 °C for 36 hours and cooled to room temperature. Stirring was continued for 4 hours. The solvent was removed under reduced pressure. The impurities in the crude product was then removed by using a short silica column with acetonitrile as the eluent. Acetone was used to dissolve and filter out the product in the silica gel. The final product (47 mg, 25% yield based on $ZnRuCl_3$) was obtained following removal of acetone under reduced pressure.

^1H NMR in Fig. S4 (500 MHz, DMSO-d_6) δ 10.19 (s, 1H), 10.04 (d, J = 4.5 Hz, 2H), 9.84 (s, 2H), 9.31 (d, J = 4.4 Hz, 2H), 9.24 (d, J = 8.1 Hz, 2H), 8.91 (d, J = 4.5 Hz, 2H), 8.71 (d, J = 4.4 Hz, 4H), 8.16 (t, J = 7.9 Hz, 2H), 8.02 (t, J = 7.8 Hz, 2H), 7.81 (t, J = 8.5 Hz, 2H), 7.73 – 7.67 (m, 2H), 7.47 (d, J = 5.5 Hz, 2H), 7.42 – 7.36 (m, 2H), 7.30 (t, J = 6.6 Hz, 2H), 7.27 – 6.98 (m, 6H), 3.95 (t, J = 7.4 Hz, 8H), 0.82 (t, J = 7.3 Hz, 8H), 0.30 (s, 36H). ^{13}C NMR in Fig. S5 (126 MHz, DMSO-d_6) δ 167.08, 159.51, 157.95, 155.05, 153.51, 152.44, 151.96, 151.34, 150.96, 149.67, 148.65, 138.39, 138.12, 132.35, 132.21, 132.12, 131.80, 131.67, 131.20, 130.99, 130.38, 130.10, 129.62, 128.74, 128.10, 127.69, 125.25, 120.22, 114.63, 108.24, 105.28, 94.35, 93.09, 65.57, 41.51, 29.67, 28.98. ESI-MS in Fig. S6: m/z = 798.24754 (z = 2).

Preparation of the Photoelectrodes. The mesoporous nanocrystalline ITO (nanoITO) electrode was prepared according to a previous report (31). The thickness of the nanoITO film was measured as 3.3 µm by a Bruker Dektak XT profilometer. The chromophores $(PhZnRu)^{2+}$ and $(RuZn)^{2+}$ were loaded by immersing the nanoITO films in acetonitrile solutions of $(PhZnRu)^{2+}$ or $(RuZn)^{2+}$ (0.20-0.23 mM) for one hour. The dyed films were then taken out of the loading solutions and dried in air for another one hour.

Computational Methods. All DFT and linear-response TDDFT calculations were performed using the Gaussian 16 software package (33). We used the PBE0 hybrid exchange correlation functional (34), which comprises the generalized gradient approximation (GGA) exchange-correlation functional of Perdew, Burke and Ernzerhe (35, 36) together with 25% of exact Hartree exchange energy. The 6-31G** basis set (37-41) was used to describe all light element atoms, and the LANL2DZ effective core potentials basis set (38, 40-43) was used for the Ru and Zn ions. All calculations were carried out with a +2 net charge for the molecules. Although the experimental UV-Vis absorption spectra were obtained with the complexes in acetonitrile solvent, all DFT and linear-response TDDFT calculations were performed in vacuum so as to be more representative of the nanoITO-$(RuZn)^{2+}$/nanoITO-$(PhZnRu)^{2+}$ heterostructures of interest, in which the molecules are not solvated. Due to the prohibitive computational expense, the calculations were performed on isolated molecules without including ITO surfaces. First, for both complexes, the ground state equilibrium geometries and electronic structures of both the $(PhZnRu)^{2+}$ and $(RuZn)^{2+}$ complexes were calculated in their singlet ground states. Next, using the 70 lowest singlet excited states of each molecular complex were computed using linear-response TDDFT. The oscillator strengths of these computed excited states, absorbing at a range of energies from ~ 1-3 eV, were then used to acquire absorption spectra for comparison to the experimental results. For both complexes, there were few optically active excited states, allowing for simple characterization of the excited state characteristics through the use of natural transition orbitals (NTOs) (27). The NTOs, which comprise linear combinations of the molecular orbitals contributing to a given excitation, are plotted as isosurfaces in Fig. 2. They represent excitations as pairs of hole and electron excited orbitals and characterize the redistribution of electron density upon photoexcitation. By plotting the NTOs, we obtain an intramolecular-level qualitative depiction of the excited state characteristics that give rise to the differences in photo-induced electronic behavior observed for the $(RuZn)^{2+}$ and $(PhZnRu)^{2+}$ complexes.

Ultrafast Transient Absorption Spectroscopy. The ultrafast transient absorption experiments were conducted with a Coherent Libra laser (45 fs pulses, 4 mJ output, 1 kHz repetition rate, 800 nm fundamental). Approximately 1.5 mJ of the fundamental was focused in a 4 m cell pressurized with argon gas to produce a continuum from 435 to 740 nm. The continuum pulse was filtered using a 4F setup built with only reflective optics and was based on a 20 cm focal length mirror and a 1200 g/mm grating. Desired portions of the continuum were selected using a motorized slit. The 455 nm pump was 22 nm at FWHM, while the 660 nm pump was 6 nm wide; the bandwidth of the 455 nm pump was increased to more closely match the power of the 660 nm pulse when incident on the sample. Both pumps were approximately 250 fs in duration. The pulse energies for the 455 nm and 660 nm pumps were 12 nJ/pulse and 22 nJ/pulse, respectively. The continuum probe pulses were generated by focusing a small fraction of the 800 nm fundamental onto a sapphire window, which were then relayed to the sample using all reflective optics. The 455 nm (660 nm) pump was focused to a roughly 300 μm (200 μm) spot. The spot size of the probe was adjusted to match that of the respective pump. The transmitted probe was detected using a CMOS array detector synchronized to the repetition rate of the laser. For a single point in the delay line, 400 differences were collected; ultrafast transient absorption signals were averaged for 30 scans of the delay line.

The time resolved data were fitted according to eqs. 1 and 2 based on the biphasic Kohlrausch-Williams-Watts (KWW) stretched exponential model (11, 44).

$$\Delta A_t = \Delta A_0 \times \exp[-(\frac{t}{\tau 0})^{\beta}] + \Delta A_0{}' \times \exp[-(\frac{t}{\tau 0'})^{\beta'}] + C \qquad \text{eq. 1}$$

$$1/\tau = [(\frac{\tau_0}{\beta}) \times \Gamma(\frac{1}{\beta})]^{-1}\text{ , } 1/\tau' = [(\frac{\tau_0'}{\beta'}) \times \Gamma(\frac{1}{\beta'})]^{-1} \qquad \text{eq. 2}$$

ΔA_t and ΔA_0 (or ΔA_0') are the absorption changes at time t and 0, respectively, after the laser pulse. β and β' are the stretching parameters. τ_0 and $\tau_0{}'$ are the characteristic KWW relaxation time constants. C is a constant generated from each fit. Γ(x) is the Gamma function. τ and τ' are the observed lifetimes, with the smaller taken as the injection lifetime.

Spectrophotometric Measurements for the Photoelectrodes Under Bias. The spectrophotometric changes of nanoITO|-$(PhZnRu)^{2+}$ and nanoITO|-$(RuZn)^{2+}$ under positive bias range were measured for the photoelectrodes in a pH 1, 0.1 M $HClO_4$ aqueous electrolyte. The experiments were carried out for the photoelectrodes under dark (spectroelectrochemical measurements) or under blue- or red-light illumination. The experimental setup for the measurements under light illumination is shown in Fig. S18. In the 2-compartment cuvette, the photoelectrode slide was placed at a 45-degree angle for facing toward both the LED irradiation light and the probe light from the spectrophotometer. The LED light was provided by the same light source as the one used in the photoelectrochemical experiments. Spectral changes were monitored by a HP 8453 Photodiode array. A CHI 660E potentiostat was used to control the applied potential to the nanoITO electrodes. The potential was stepped at every 20 mV for 200 seconds with UV-Vis absorption spectrum taken at each step. The observed spectral changes were corrected via background subtraction with the corresponding absorptive changes from the bare nanoITO electrode. The spectroelectrochemical measurements under negative bias range were done for the photoelectrodes in pH 13, 0.1 M NaOH aqueous electrolyte.

Photocurrent Measurements. A custom-made, two-compartment photoelectrochemical cell was used for photocurrent measurements with the photoelectrodes, nanoITO|-$(PhZnRu)^{2+}$ and nanoITO|-$(RuZn)^{2+}$. The electrolyte contained 0.77 mM ascorbic acid and 0.77 mM 4,4'-dipyridyl disulfide in 0.1 M, pH 4.5 acetate (0.1 M) buffer. During experiments, the nanoITO electrode was immersed in one compartment filled with the argon-degassed redox buffer. The other compartment contained a platinum mesh counter electrode and a Ag/AgCl reference electrode, both of which were immersed in the argon-degassed redox buffer. A CHI 601D potentiostat was used to supply the applied bias (0.20 V vs NHE) for the photoelectrodes and record the current–time signals. The photoelectrodes were irradiated by red (λ_{max}: 650 nm, 20 nm FWHM) or blue (λ_{max}: 455 nm, 20 nm FWHM) light with a solid-state light source (Lumencor, Inc.; beam diameter: 0.8 cm; output: 10-12 mW/cm^2).

Nanosecond Transient Absorption Spectroscopy. The nanosecond transient absorption measurements were performed with a nanosecond spectrophotometer as reported previously (44). During the experiments, film samples with an area of 1.0 cm^2 were placed in a 1 cm pathlength quartz cuvette filled with pH 4.5, 0.1 M acetate buffer. Single wavelength TA changes of the samples upon excitation by 480 nm (2.0 mJ/pulse) or 670 nm (1.0 mJ/pulse) laser pulses were monitored by using a digital oscilloscope.

Electrochemical Characterization of (PhZnRu)$^{2+}$ and (RuZn)$^{2+}$. The cyclic voltammograms of (PhZnRu)$^{2+}$ and (RuZn)$^{2+}$ were acquired by scanning the chromophores in argon-degassed acetonitrile solutions with 0.1 M tetrabutylammonium hexafluorophosphate. A typical three electrode cell was used with glassy carbon as the working electrode, Ag/AgCl as the reference electrode, and Pt mesh as the counter electrode.

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Author contributions: T.J.M. and B.S. conceived the research. All authors contributed to the experimental designs. B.S., A.N., O.F.W., N.F.P., Y.L. and N.Z. performed the experiments and measurements. D.C.Y. and Y.K. carried out the DFT and TDDFT calculation. O.F.W., N.Z. and A.M.M. carried out the ultrafast TA measurements. T.J.M. and B.S. wrote the paper with contributions from all authors.

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