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Photoinduced Electron Transfer in an Anthraquinone–$[Ru(bpy)_3]^{2+}$–Oligotriarylamine–$[Ru(bpy)_3]^{2+}$–Anthraquinone Pentad

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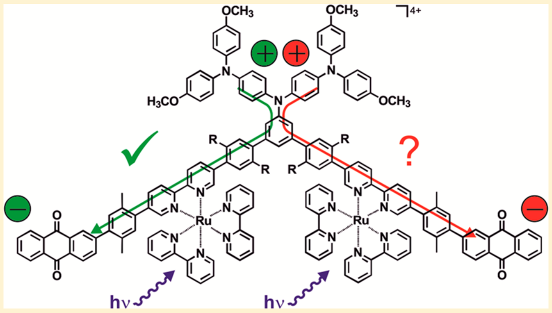
Ⓢ *Supporting Information*

ABSTRACT: A molecular pentad comprised of a central multielectron donor and two flanking photosensitizer-acceptor moieties was prepared in order to explore the possibility of accumulating two positive charges at the central donor, using visible light as an energy input. Photoinduced charge accumulation in purely molecular systems without sacrificial reagents is challenging, because of the multitude of energy-wasting reaction pathways that are accessible after excitation with two photons. As expected, the main photoproduct in our pentad is a simple electron–hole pair, and it is tricky to identify the desired two-electron oxidation product on top of the stronger signal resulting from one-electron oxidation.



INTRODUCTION

Electron–hole pairs have been observed after the photoexcitation of many different dyads,[1] triads,[2] tetrads,[3] and pentads.[4] However, light-driven accumulation of multiple electrons or holes on a given molecular unit is much less straightforward, at least when aiming at charge accumulation without using sacrificial reagents.[5] At present, only a handful of prior studies have addressed this subject successfully.[6]

Charge accumulation is necessary for artificial photosynthesis, because fuel-forming reactions such as H_2 production or CO_2 reduction require multiple redox equivalents.[5b,7] Therefore, it is desirable to gain knowledge on how light-driven charge accumulation can be performed efficiently, ideally without sacrificial donors or acceptors. This was the purpose of the research presented in this paper.

The molecular pentad in Scheme 1 is comprised of a central oligotriarylamine (OTA) donor that is easily oxidized up to three times. The OTA multielectron donor is connected to two $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) photosensitizers, each of which bears an anthraquinone (AQ) acceptor. In principle, AQ can accept two electrons; however, here, we aimed to explore whether photoexcitation of both $[Ru(bpy)_3]^{2+}$ units could lead to a charge-separated state in which OTA has been oxidized to its dicationic state (OTA^{2+}) while both AQ units have been reduced to their monoanionic form (AQ^-). To the best of our knowledge, such photodriven hole accumulation in a purely molecular system has never been achieved without sacrificial electron acceptors.

RESULTS AND DISCUSSION

Synthesis. The key ligand for the AQ–Ru^{II}–OTA–Ru^{II}–AQ pentad from Scheme 1 was synthesized in 18 steps using standard C–C and N–C coupling reactions, as described in detail in the Supporting Information. The final compound was characterized by nuclear magnetic resonance (NMR) spectroscopy, high-resolution electron spin ionization (ESI) mass spectrometry, and by elemental analysis.

Electrochemistry. Cyclic voltammetry was used to determine the reduction potentials of the individual components of the pentad. Measurements were performed in dry CH_3CN at 20 °C and provided the results shown in Table 1. Voltammograms and further experimental details are given in the Supporting Information. OTA is oxidized reversibly to its monocationic and dicationic forms at −0.01 and 0.23 V vs Fc^+/Fc, which is consistent with prior studies.[6b,8] The formation of OTA^{3+} at 0.65 V is quasi-reversible, as reported earlier.[6b,8] The redox potentials of the AQ and the $[Ru(bpy)_3]^{2+}$ components of the pentad are similar to those found for neat anthraquinone or $[Ru(bpy)_3]^{2+}$ under identical conditions.[9]

Based on these potentials, excitation of the pentad at one of its two photosensitizer units should lead to a charge-separated state comprised of OTA^+ and AQ^-, similar to what was observed in structurally related triads.[2l,10] The resulting AQ^-–Ru^{II}–OTA^+–Ru^{II}–AQ state is expected to be ca. 1.26 eV above the initial (ground) state. Excitation of the second photosensitizer unit can then potentially lead to reduction of the second AQ unit and oxidation of OTA^+ to OTA^{2+}. The resulting AQ^-–Ru^{II}–OTA^{2+}–Ru^{II}–AQ^- state is expected to be ca. 2.74 eV above the ground state, which is much lower in energy than a hypothetical AQ^{2-}–Ru^{II}–OTA^{2+}–Ru^{II}–AQ state in which two electrons are located on the same AQ unit. In the following optical spectroscopic studies, we searched for the AQ^-–Ru^{II}–OTA^{2+}–Ru^{II}–AQ^- photoproduct.

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Scheme 1. Chemical Structure of the AQ–Ru^{II}–OTA–Ru^{II}–AQ Pentad

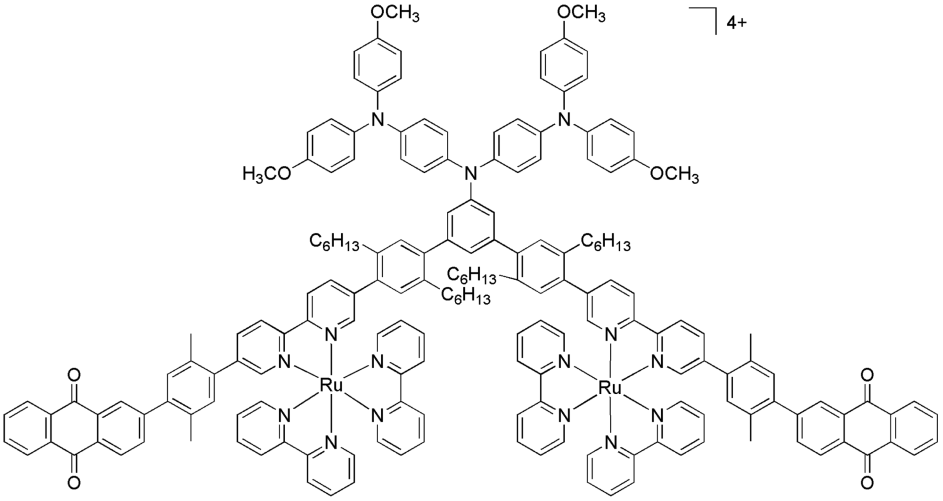

Table 1. Redox Potentials (V vs. Fc$^+$/Fc) in CH_3CN[a]

	pentad	$[Ru(bpy)_3]^{2+}$	AQ[b]
Ru(III/II)	0.91	0.90	
$OTA^{+/0}$	−0.01		
$OTA^{2+/+}$	0.23		
$OTA^{3+/2+}$	0.65		
$bpy^{0/-}$	−1.67	−1.72	
$bpy^{0/-}$	−1.92	−1.92	
$bpy^{0/-}$	−2.20	−2.17	
$AQ^{0/-}$	−1.25		−1.23
$AQ^{2-/-}$	−2.0[c]		−1.77

[a] Measured in the presence of 0.1 M $TBAPF_6$ as a supporting electrolyte using scan rates of 0.1 V/s. [b] From ref 9a for neat 9,10-anthraquinone in DMF; potential converted from SCE to Fc$^+$/Fc, following ref 11. [c] Irreversible.

UV–vis Spectroscopy and Chemical Oxidation. The black trace in Figure 1a is the absorption spectrum of the pentad in neat CH_3CN at 20 °C. Absorption bands with maxima at 455, 324, and 250 nm are attributable to $[Ru(bpy)_3]^{2+}$, AQ, and OTA components, respectively; an additional band at 290 nm is due to bpy-localized $\pi-\pi^*$ transitions. The red trace was measured in the presence of 2000 equiv of *N,N′*-diphenylthiourea, which is able to form tight hydrogen-bonds to quinone radical anions.[12] We anticipated that this might facilitate AQ reduction, potentially leading to longer-lived charge-separated states and increased chances of observing the desired AQ$^-$–Ru^{II}–OTA^{2+}–Ru^{II}–AQ$^-$ photoproduct.[2l,8b,13] Brönsted acids or the strong hydrogen-bond donor hexafluoroisopropanol lead to oxidation of OTA in darkness and, therefore, were not considered further.

The UV-vis spectral changes occurring in the course of chemical oxidation of OTA to OTA$^+$ and OTA^{2+} by $Cu(ClO_4)_2$ ($E^0 = 0.57$ V vs Fc$^+$/Fc in CH_3CN)[11,14] are shown in Figure 1b. The UV-vis spectrum measured prior to adding any oxidant served as a baseline. The blue and green traces were measured after addition of 1.0 and 2.5 equiv of $Cu(ClO_4)_2$ and are attributed to OTA$^+$ and OTA^{2+}, respectively, which is consistent with prior studies.[6a,b,8b,c] These chemical oxidation experiments demonstrate that OTA$^+$ and OTA^{2+} are best distinguishable from each other in the near-infrared (NIR) spectral range. Therefore, the nanosecond transient absorption studies reported below focused on the detection of a band at 1130 nm (attributable to OTA^{2+}) on top of a band at 1315 nm (caused by OTA$^+$).

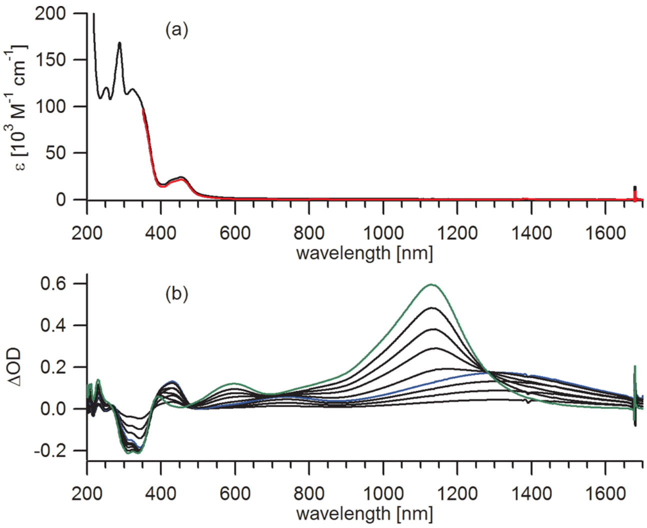

Figure 1. (a) UV-vis absorption spectra obtained from 10^{-5} M solutions of the pentad in CH_3CN (black trace represents data in neat solvent; red trace represents data in the presence of 2000 equiv of *N,N′*-diphenylthiourea. (b) UV-vis difference spectra measured after addition of increasing amounts of $Cu(ClO_4)_2$ to a 10^{-5} M solution of the pentad in CH_3CN; the spectrum prior to adding any Cu(II) oxidant served as a baseline. Blue trace represents data measured after the addition of 1.0 equiv of oxidant, spectrum attributed to OTA$^+$; green trace represents data measured after the addition of 2.5 equiv of oxidant, spectrum attributed to OTA^{2+}.

Nanosecond Transient Absorption. A deaerated 10^{-5} M solution of the pentad containing 2000 equiv of *N,N′*-diphenylthiourea was excited with laser pulses of ~10 ns duration at 532 nm, resulting in the transient absorption spectra shown in Figure 2a. The black and blue traces were obtained using pulse energies of 10 and 60 mJ, respectively. We estimate that this corresponds to a flux of ca. ~4 and ~24 photons per molecule and pulse, respectively, and therefore multiphoton processes should be possible.

Both transient absorption spectra in Figure 2a exhibit prominent bands at 1280 and 410 nm, which are compatible with the predominant formation of OTA$^+$. An additional band at 540 nm in transient absorption can be attributed to

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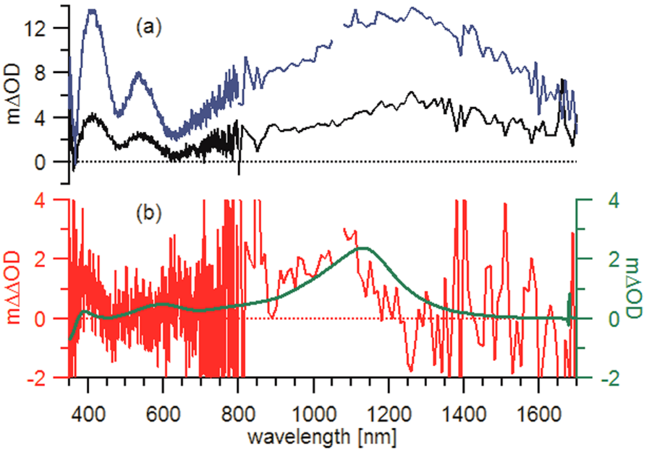

Figure 2. (a) Transient absorption spectra measured after excitation at 532 nm with laser pulses of ~10 ns duration. Both spectra were time-integrated over a detection period of 200 ns immediately after excitation. Black trace: excitation with 10 mJ/pulse; blue trace: excitation with 60 mJ/pulse. (b) Red trace: Difference spectrum obtained after subtraction of the black trace in panel (a) from the blue trace in panel (a); prior to the subtraction, the two spectra from panel (a) were scaled to identical intensities at 1285 nm (see text for further details). Green trace represents the UV-vis difference spectrum associated with the formation of OTA^{2+} (green trace from Figure 1b).

AQ^{-},[10a,b,15] and, hence, it is clear that the majority photoproduct is the $AQ^{-}-Ru^{II}-OTA^{+}-Ru^{II}-AQ$ state. This is not unexpected because only a fraction of all pentads that have absorbed a first photon will also absorb a second photon.[6a−c] The transient absorption signals at 410, 540, and 740 nm (Supporting Information) decay with a lifetime of 160 ns, irrespective of whether *N*,*N*′-diphenylthiourea is present (Table 2 and Figure S2). Importantly, the $AQ^{-}-Ru^{II}-OTA^{+}-Ru^{II}-AQ$ state is formed within 10 ns, hence the possibility for absorption of a (second) photon from this state within the same laser pulse is indeed given.

Table 2. Lifetimes of Photoproducts in Deaerated CH_3CN at 20 °C

	τ_0 [ns]	τ_1 [ns]
neat, 10 mJ	160	
2000 eq thiourea, 10 mJ	160	
2000 eq thiourea, 60 mJ	100	290

In our search of evidence for the $AQ^{-}-Ru^{II}-OTA^{2+}-Ru^{II}-AQ^{-}$ state, we subtracted the black trace from the blue trace in Figure 2a, in order to obtain a difference spectrum in which the dominant contribution from the simple AQ^{-}/OTA^{+} electron−hole pair is eliminated. For this purpose, the two spectra in Figure 2a were scaled to equal intensities at 1285 nm, which is an isosbestic point appearing in the course of the formation of OTA^{+} and OTA^{2+} (Figure 1b). The result is shown as a red trace in Figure 2b, together with the UV-vis difference spectrum obtained for OTA^{2+} in the chemical oxidation experiment (green trace from Figure 1b). We note that there is indeed some agreement between the two difference spectra in Figure 2b, particularly in the NIR spectral range (~1100 nm) and near 400 nm where OTA^{2+} has characteristic absorption bands. This observation suggests that a small fraction of the desired $AQ^{-}-Ru^{II}-OTA^{2+}-Ru^{II}-AQ^{-}$ state is indeed formed.

Transient absorption decays measured after excitation with pulse energies of 60 mJ are biexponential (see Table 2 and Figure S2). In principle, such behavior is compatible with two independently decaying photoproducts such as the $AQ^{-}-Ru^{II}-OTA^{+}-Ru^{II}-AQ$ majority state and the desired $AQ^{-}-Ru^{II}-OTA^{2+}-Ru^{II}-AQ^{-}$ state. However, the relative contributions of the two decay components are roughly 60% (τ = 290 ns) to 40% (τ = 100 ns) at all detection wavelengths (Figure S2 in the Supporting Information), which would imply a large contribution from the desired $AQ^{-}-Ru^{II}-OTA^{2+}-Ru^{II}-AQ^{-}$ state to the overall decay. Therefore, it seems more likely that the biexponential decay behavior at high pulse energies is an effect that is not directly related to the charge-accumulated state. It is conceivable that this is a thermal effect.

Pump−pump−probe experiments in which a first excitation pulse at 532 nm was followed by a second excitation pulse at 480 nm (with a delay time of 10−20 ns) did not provide clearer evidence for the formation of OTA^{2+} either (Figure S3 in the Supporting Information).

As noted above, the desired $AQ^{-}-Ru^{II}-OTA^{2+}-Ru^{II}-AQ^{-}$ state is 2.74 eV above the ground state, and, consequently, many decay channels to energetically lower states do potentially exist. Therefore, one might expect this state to be rather short-lived, and, for this reason, transient absorption studies with higher temporal resolution were performed.

Femtosecond Transient Absorption. Excitation of the pentad in deaerated CH_3CN at 385 nm using a setup with an ~150 fs instrument response function[16] yielded the transient absorption spectra in Figures 3a and 3b. Differences between the spectra obtained at low (0.4 mJ/cm^2, Figure 3a) and high excitation densities (8.0 mJ/cm^2, Figure 3b) are observed between 470 nm and 540 nm. The time evolution of the transient absorption at low excitation density could be well reproduced by global target analysis, assuming three consecutive exponential steps A → B → C → D and yielded the species-associated decay spectra (SADS)[17] shown in Figure 3c.

Precise interpretation of these species/states is not straightforward, but step A most probably corresponds to the ^{3}MLCT state of the $[Ru(bpy)_3]^{2+}$ sensitizer, although some contribution from the triplet excited state of AQ cannot be excluded.[18] On the other hand, species C is more compatible with $AQ^{-}-Ru^{II}-OTA^{+}-Ru^{II}-AQ$ than with the desired $AQ^{-}-Ru^{II}-OTA^{2+}-Ru^{II}-AQ^{-}$ state. Unfortunately, measurements in the NIR spectral range, which would permit distinguishing more clearly between between OTA^{+} and OTA^{2+}, cannot be performed on the femtosecond setup. The spectrum of state B resembles that of state C but has a smaller amplitude. This suggests that state B might be associated with a reaction intermediate (for example, a charge-separated state with the electron or the hole on the sensitizer). In any case, these data indicate that the quenching of the excited sensitizer (A → B) occurs within a few picoseconds, whereas the $AQ^{-}-Ru^{II}-OTA^{+}-Ru^{II}-AQ$ state (C) is populated within <400 ps.

At high excitation density, two additional steps must be added to properly account for the observed transient absorption dynamics, with the SADS and time constants shown in Figure 3d. The last two species, D and E, have similar spectra and lifetimes as B and C in the low intensity measurements, indicating that the $AQ^{-}-Ru^{II}-OTA^{2+}-Ru^{II}-AQ^{-}$ state is still not populated. The SADS of species A, B, and C in the high-intensity measurements are all very similar, except for their amplitude, and resemble the SADS of state A measured at low intensity. This indicates that these four spectra

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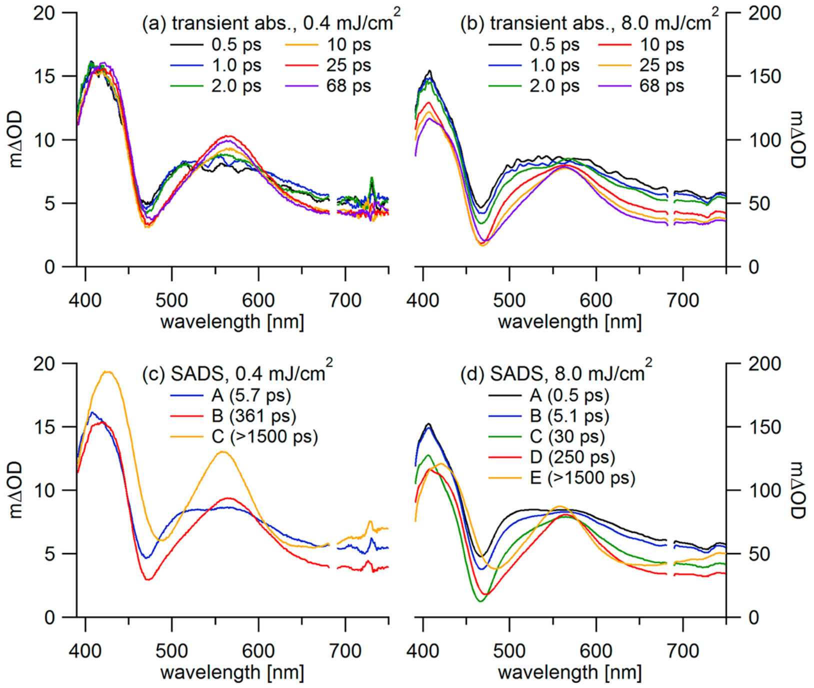

Figure 3. Transient absorption spectra recorded at different delay times after excitation at 385 nm with femtosecond laser pulses at (a) low excitation densities and (b) high excitation densities.[16] (c, d) Species-associated decay spectra (SADS) obtained from global target analyses of the data in panels (a) and (b), assuming a series of three consecutive exponential steps (panel (c)) or five consecutive exponential steps (panel (d)).

are due to the same species/state, most probably $[Ru(bpy)_3]^{2+}$ in the ^{3}MLCT state, and that, at high excitation density, the decay of this state is not single exponential. Such dependence on the excitation intensity is typical of exciton annihilation, and has been observed with many multichromophoric systems and aggregates.[19] In the present case, triplet−triplet annihilation between two $[Ru(bpy)_3]^{2+}$ units in the ^{3}MLCT state is the most probable origin of the nonexponential decay at higher excitation density. Such process is strongly detrimental to efficient accumulative electron transfer, but can be minimized by using sufficiently long excitation pulses, so that the first photoinduced charge separation process occurs before the second sensitizer is excited. This is clearly not possible with the 100 fs pulses used here for the femtosecond measurements, because quenching of the $[Ru(bpy)_3]^{2+}$ in the ^{3}MLCT state occurs within a few picoseconds (step A → step B in Figure 3a). In the nanosecond measurements, pulses longer by a factor 10^5 are used, and therefore the probability for a pentad to have two excited $[Ru(bpy)_3]^{2+}$ units, none of which has yet participated in photoinduced electron transfer, is very low, even with 60 mJ pulses. In the latter case, even though the energy per pulse is large, the irradiance is only 84 MW/cm^2 (2.25×10^{14} photons/cm^2/ps), compared to 80 GW/cm^2 (1.55×10^{17} photons/cm^2/ps) with the high-intensity femtosecond measurements. This could explain why the double charge-separated state, $AQ^-{-}Ru^{II}{-}OTA^{2+}{-}Ru^{II}{-}AQ^-$, might be observed in the nanosecond measurements but not in the femtosecond studies.

SUMMARY AND CONCLUSIONS

Not surprisingly, photoexcitation of the pentad from Scheme 1 in CH_3CN leads primarily to the population of a charge-separated state in which one AQ is reduced and OTA is oxidized. This state is formed rapidly (<1 ns) and it lives for 160 ns in deaerated CH_3CN at 20 °C. When using high excitation powers in nanosecond transient absorption spectroscopy, a weak signal that is compatible with the formation of OTA^{2+} becomes detectable, suggesting that small amounts of the desired $AQ^-{-}Ru^{II}{-}OTA^{2+}{-}Ru^{II}{-}AQ^-$ state are indeed formed. However, it has not been possible to corroborate this interpretation by exploring the excitation power dependence of this weak signal, or by measuring its temporal evolution. We conclude that there is some evidence for photodriven charge accumulation, but the case is not clear-cut.

As noted in the Introduction, we are unaware of prior studies that have reported on light-driven hole accumulation in purely molecular systems without using sacrificial electron acceptors. The reason why this is such a tricky task is the multitude of unproductive (energy-wasting) reaction pathways that are available after excitation with two photons. These pathways include thermal charge-recombination, energy transfer processes, and triplet−triplet annihilation events. Moreover, once the $AQ^-{-}Ru^{II}{-}OTA^+{-}Ru^{II}{-}AQ$ state is formed, excitation of the second ruthenium photosensitizer could lead to reduction of OTA^+ to OTA, because OTA^+ is a good electron acceptor. Understanding the basic principles of photodriven charge accumulation remains an important challenge, in view of artificial photosynthesis.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b02757.

Syntheses and product characterization data, as well as additional electrochemical and optical spectroscopic data (PDF)

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Notes

The authors declare no competing financial interest.

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