

Electron-Exchange-Assisted Photon Energy Up-Conversion in Thin Films of π -Conjugated Polymeric Composites

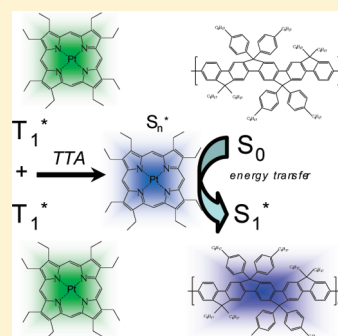
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 Supporting Information

ABSTRACT: The mechanism of triplet–triplet annihilation (TTA)-induced up-converted (UC) delayed luminescence is studied in two different binary organic systems consisting of platinum(II) octaethyl porphyrin (PtOEP) mixed with either poly(fluorene) (PF26) or ladder-type pentaphenylene (LSPh). Cyclic voltammetry and differential pulse voltammetry are employed for estimating the ionization potentials of PtOEP and LSPh. Delayed luminescence spectroscopy sets the energy of the lowest excited triplet state of LSPh 0.20 eV higher than the triplet state of PtOEP (1.90 eV). The different phosphorescence PtOEP lifetime indicates differences in PtOEP aggregation in the polymer matrices. The presented results propose that the difference in the relative intensities of the delayed UC luminescence is determined by the difference between the ionization potentials of PtOEP and the polymer matrix. In the solid state, the electric-field-induced quenching of the delayed LSPh UC luminescence suggests the formation of an intermediate charge-transfer state after the TTA within the PtOEP domains.

SECTION: Kinetics, Spectroscopy



The process of low-photon energy up-conversion in multi-component blends is attracting increasing attention because of its potential in practical applications, for example, in the sensitization of solar cell devices. Thin solid films of photon up-converting layers can be optically coupled to photovoltaic devices to increase the efficiency of photocurrent generation in the spectral range where absorption of the photoactive layer itself is inefficient.^{1–3}

In particular, for the case of solid-state polymer/sensitizer composites, photon energy up-conversion can be initiated by the process of triplet–triplet annihilation (TTA).^{4–12} Absorption of low-energy photons by the composite populates the triplet manifold in one of the composite components. Following TTA, a higher lying excited state is populated and a high-energy photon is emitted. (See Figure 1 in ref 13.)

Organic photon up-converters are layers of polymeric composites that typically consist of small molecular guests dispersed in π -conjugated polymeric matrices. The former are defined as sensitizers (S) that harvest photons of low energy, and the latter are defined as activators (A) that accept the energy of S and generate up-converted luminescence.¹⁴ Selective photoexcitation of the A/S photoactive mixture in the absorption range of S results in population of the triplet state in S (T_S) via fast intersystem crossing. The preferential excited-state pathway for TTA is then determined by the difference between the energy of T_S (E_{T_S}) and the triplet state of T_A (E_{T_A}).^{13,15} If $E_{T_S} \geq E_{T_A}$, then efficient heteromolecular triplet energy migration¹⁶ is possible from T_S to T_A . Following this triplet–triplet energy transfer, TTA may take place in the triplet manifold of A that subsequently

emits its characteristic fluorescence-like delayed luminescence.⁷ If $E_{T_S} < E_{T_A}$, then triplet migration from S to A is inhibited and TTA takes place in the triplet manifold of S that results in the formation of a higher lying state.⁵ From this state, energy or charge transfer may take place between the S and A components of the composite and the generation of delayed up-converted luminescence of A can be observed. The nature of the energy transfer step between the higher lying excited state of S and A is still not fully understood, and it was recently proposed that it takes place either via an electron-exchange energy transfer step between S and A⁹ or via TTA between S–A exciplex species.¹⁷ More recently, it was suggested that in multicomponent systems where $E_{T_S} < E_{T_A}$ the process of TTA-mediated low-photon energy up-conversion operates based on an entropically driven triplet energy migration.¹⁸

In this Letter, we present evidence in favor of the electron-exchange energy mechanism; in particular, we suggest that a charge-transfer mediated energy transfer process between S and A can explain the generation of low-photon energy up-converted fluorescence in systems where $E_{T_S} < E_{T_A}$. For our study, we use 2,3,7,8,12,13,17,18-octaethyl-porphyrinato Pt(II) (PtOEP) as a sensitizer, whereas as activators, we use either poly[9,9-bis(ethyl-hexyl)fluorene] (PF26) or derivatives of a poly(ladder-type pentaphenylene). In particular, the partially arylated poly(ladder-type pentaphenylene) (LSPh)¹⁹ and the fully arylated

Received: June 3, 2011

Accepted: July 7, 2011

Published: July 07, 2011

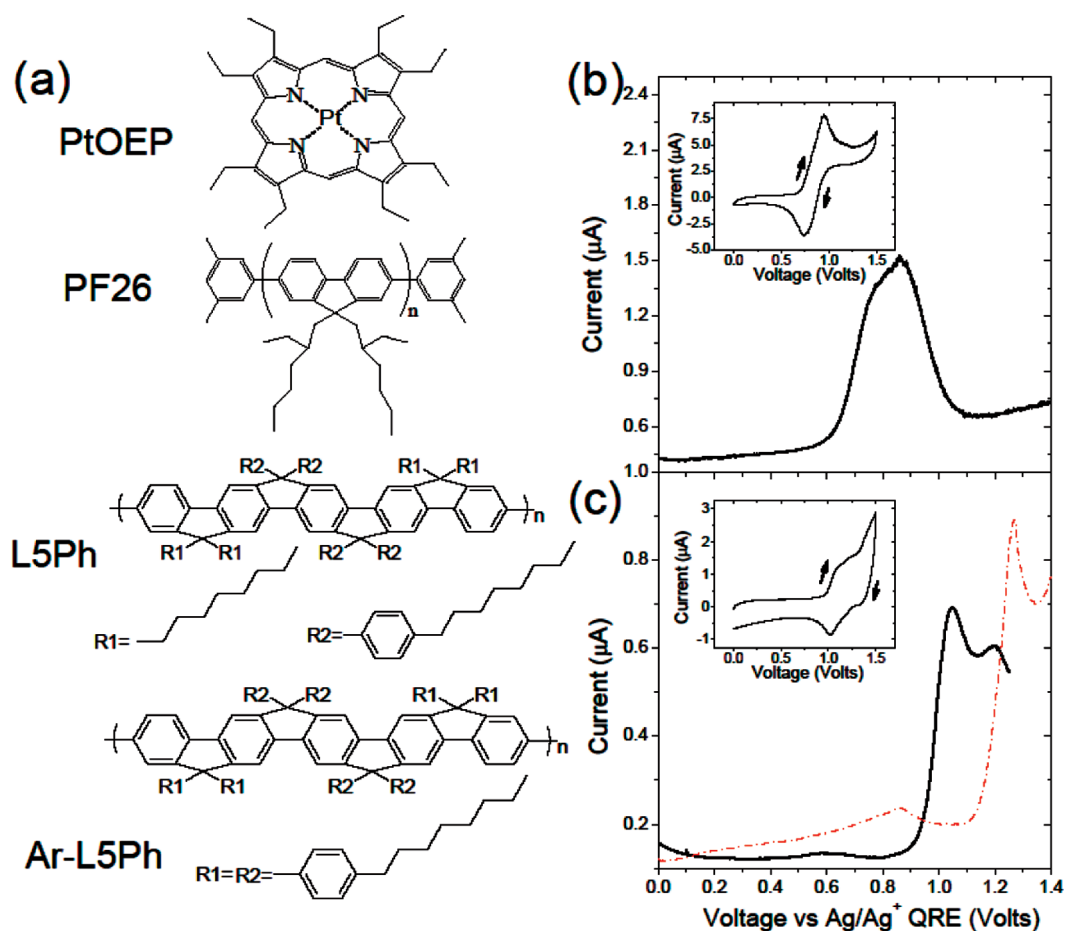


Figure 1. (a) Chemical structures of the materials used in the present study. The differential pulse voltammetry and cyclic voltammetry oxidation (inset) waves for solutions of (b) PtOEP and (c) L5Ph. Ag/Ag⁺ was used as the quasi reference electrode (QRE). The red dashed-dotted line in part c depicts the oxidation wave of PF26.

poly(ladder-type pentaphenylene) (Ar-L5Ph)²⁰ derivatives are studied. The chemical structures of the materials used are shown in Figure 1a. The first triplet excited state of PtOEP (T_{PtOEP}) corresponds to an energy of $E_{T_{\text{PtOEP}}} = 1.90$ eV.²¹ Previous spectroscopic studies have determined the absolute value of the first triplet excited state of PF26 (T_{PF26}) based on the direct detection of phosphorescence. In particular, the determination of $E_{T_{\text{PF26}}}$ varied depending on the experimental conditions, and the detection of PF26 phosphorescence was possible only at temperatures as low as 77 K. For dilute solutions of PF26, T_{PF26} corresponds to $E_{T_{\text{PF26}}} = 2.15$ eV,^{22,23} whereas for the case of PF26 thin films, it was found that $E_{T_{\text{PF26}}} = 2.10$ – 2.15 eV.^{22,24}

We have previously shown that solid-state films of the L5Ph/PtOEP composite exhibit superior up-converted luminescence efficiency in comparison with the PF26/PtOEP system.²⁵ This observation was partially interpreted based on the observation of reduced reabsorption of the L5Ph up-converted luminescence by the excited states of PtOEP. Herein we further explain that L5Ph exhibits more efficient up-converted luminescence both in solution and in the solid state because of the favorable energy of the highest occupied molecular orbital (HOMO) that allows efficient electron-exchange between L5Ph and PtOEP after the TTA process between PtOEP molecules.

We have determined the energies of the HOMO levels for PtOEP, PF26, and L5Ph in CH₂Cl₂ solution by performing cyclic

Table 1. $E_{1/2}$ and HOMO Values Together with the Energy of T_1 Level of All Materials Studied

system	$E_{1/2}$ (volts) ^a	HOMO (eV) ^a	T_1 (eV) ^b
PtOEP	0.75	4.98	1.90 ²¹
PF26	1.27	5.50 ²⁶	2.15 ²⁴
L5Ph	1.06	5.29	2.10

^a $E_{1/2}$ differential pulse voltammetry data of PtOEP, PF26, and L5Ph in solution together with the HOMO values extracted as described in the text. ^b Value for the triplet energy level T_1 of the studied materials in the solid state: for L5Ph, T_1 is determined by the delayed luminescence data of Figure 2

voltammetry (CV) and differential pulse voltammetry (DPV) experiments. Our electrochemistry experiment aimed at identifying the relative energetic positions of the HOMO levels of the studied materials. For this reason, the measured electrochemical potentials were converted to HOMO energies by using the PF26/PF26⁺ (HOMO = 5.50 eV)²⁶ as the reference. The half-wave oxidation potential $E_{1/2}$ is calculated according to $E_{1/2} = E_{\text{peak}} + \Delta E/2$,²⁷ where E_{peak} is the peak value of the corresponding DPV redox wave. Figure 1b,c present the DPV oxidation waves of PtOEP, L5Ph, and PF26 materials. For our reference material PF26, the $E_{1/2}$ value of 1.27 eV is in agreement with the previously reported values of

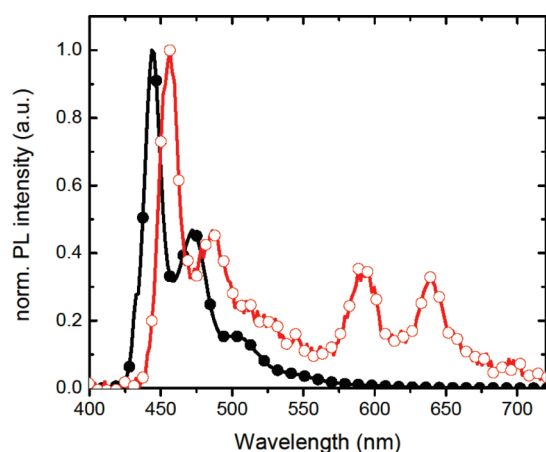


Figure 2. Delayed luminescence spectrum of an Ar-LSPH film at 77 K (open symbols). The spectrum was recorded 1 μ s after photoexcitation over a 10 ms integration window. The room-temperature prompt luminescence spectrum (filled symbols) is also shown. Both spectra were acquired after photoexcitation of the sample at 430 nm in a dynamic vacuum of 10^{-5} mbar.

1.2 eV versus Ag.²⁶ Table 1 presents the $E_{1/2}$ and HOMO values together with the energy of T_1 level of all materials studied.

We have performed low-temperature (77 K) delayed luminescence (DL) measurements (in the microsecond time range)^{24,28} on an Ar-LSPH film cast from toluene. DL spectra were recorded with microsecond delays after optical excitation of the film at 430 nm. An example of these measurements is shown in Figure 2, where the DL spectrum was recorded 1 μ s after photoexcitation and integrated over a time window of 10 ms. For reasons of comparison, the prompt PL spectrum of the same film at room temperature is also depicted. Two spectral contributions can be identified in the DL spectrum of Ar-LSPH. In the high-energy part of the DL spectrum, the luminescence band centered at 456 nm is assigned to the delayed fluorescence from the S_1 electronic state of Ar-LSPH ($S_0 \leftarrow S_1$ transition). In comparison with the room-temperature prompt fluorescence spectrum, the DL $S_0 \leftarrow S_1$ emission band exhibits a 77 meV red shift that can be attributed to the downhill spectral diffusion process or to the increased planarization of the Ar-LSPH at 77 K. An additional luminescence band is seen in the low-energy part peaking at 590 nm that is not present in the prompt fluorescence spectra of Ar-LSPH at room temperature. This emissive feature is assigned to the phosphorescence of Ar-LSPH ($S_0 \leftarrow T_1$ transition). Both $S_0 \leftarrow S_1$ and $S_0 \leftarrow T_1$ luminescence bands bear a vibronic progression of 160 meV that is the characteristic signature of the C=C stretch of the phenyl rings of the Ar-LSPH polymer backbone.²² On the basis of the peak of the phosphorescence emission shown in the DL spectra of Figure 2, the triplet-state energy of Ar-LSPH films at 77 K is determined to be $E_{T_{\text{Ar-LSPH}}} = 2.10$ eV. Because the pendant groups of the poly(ladder-type pentaphenylene) derivatives are not in conjugation with the main polymer backbone, no differences are expected in the triplet energy level of LSPH and Ar-LSPH. This is further supported by the time-integrated UV-vis and PL spectra of films made by these materials. In the solid state, both polymers exhibit the same maxima of UV-vis absorption and PL emission at around 435 nm and at 445 nm, respectively.^{19,20}

The time-integrated PL properties of PF26/PtOEP and LSPH/PtOEP solutions in toluene were also investigated. For

both solutions, the polymer concentration was 0.25 mg/mL and the wt % PtOEP content was 20%. As Figure 3a shows, comparable PL intensities were received for both polymer/PtOEP solutions after optical excitation at 390 nm with a conventional spectrofluorimeter. For the same solutions, we have performed time-integrated PL measurements for laser excitation at 532 nm with 1 kW/cm² photoexcitation intensity.²⁵ Figure 3b presents the spectra of the PF26/PtOEP and LSPH/PtOEP systems where the up-converted luminescence of PF26 and L-PSh is clearly observed. Despite the similar PL intensities when the solutions are excited at 390 nm (Figure 3a), the intensity of the up-converted luminescence is significantly different. Comparing the spectrally integrated up-converted PL values, we find that LSPH exhibits more than 10 times stronger up-converted PL than PF26. The comparable PL intensities of the two systems when excited at 390 nm (Figure 3a) suggest that quenching of the up-converted luminescence due to energy transfer back to PtOEP⁹ is expected to take place on a similar magnitude for both systems. Therefore, the different up-converted luminescence intensities of PF26 and LSPH indicate the occurrence of an unidentified process that selectively limits the efficiency of the TTA-induced up-converted PL generation efficiency in the PF26/PtOEP system but not in the LSPH/PtOEP system. It was recently suggested that photon up-conversion in systems like PF26/PtOEP and LSPH/PtOEP may be assisted by the coaggregation of the sensitizer and the activator components of the system.^{9,17} For the case of LSPH/PtOEP solution, we consider the formation of coaggregate LSPH-PtOEP species to be improbable because of the steric hindrance caused by the bulky pendant groups that protect the LSPH backbone and limit the possibility for π - π interaction with PtOEP. No indication for ground-state interaction was found in the UV-vis spectra of the PF26/PtOEP and LSPH/PtOEP solutions after comparing them with the corresponding spectra of the PF26 and LSPH polymers (Supporting Information). However, we cannot exclude the possibility that PtOEP could interact with the aromatic side chains of LSPH or that electronic interactions between the solution components may take place in the excited state.

To explore further the origin of the different up-converted PL efficiency in the two systems, we have performed time-resolved measurements of the PtOEP phosphorescence and polymer up-converted luminescence in thin films of LSPH/PtOEP and PF26/PtOEP. The employed experimental setup has been previously described.⁹ For both systems, the PtOEP content was kept at 3 wt %. Figure 3c,d presents the decay transients of PtOEP phosphorescence (Ph_{PtOEP}) and polymer up-converted luminescence for each system. For PF26/PtOEP film, the lifetime values of Ph_{PtOEP} - and PF26-delayed up-converted luminescence (UC_{PF26}) were 58 and 12 μ s, respectively. Interestingly, for the case of the LSPH/PtOEP film, the lifetime values of Ph_{PtOEP} and LSPH delayed up-converted (UC_{LSPH}) were 29 and 5 μ s respectively. The two-fold reduced Ph_{PtOEP} value of the LSPH/PtOEP film could suggest that energy migration operates between the triplet manifolds of PtOEP (T_{PtOEP}) and LSPH (T_{LSPH}). We exclude this option because of triplet energy level mismatch between these two materials; on the basis of the results shown in Figure 1, we derive $E_{T_{\text{LSPH}}} - E_{T_{\text{PtOEP}}} = 200$ meV \gg kT. Moreover, it was previously shown that in the PF26/PtOEP system where $E_{T_{\text{PF26}}} - E_{T_{\text{PtOEP}}} = 250$ meV the process of TTA-driven photon up-conversion is enhanced at low temperatures;⁵ therefore, any endothermic process during the process of triplet

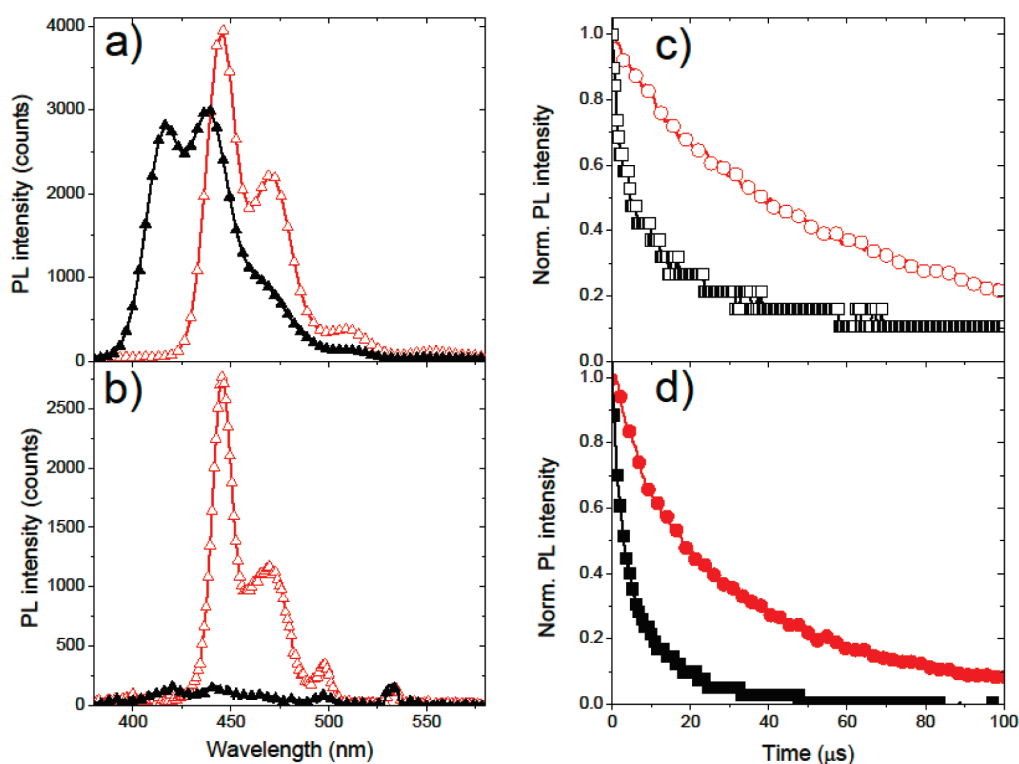


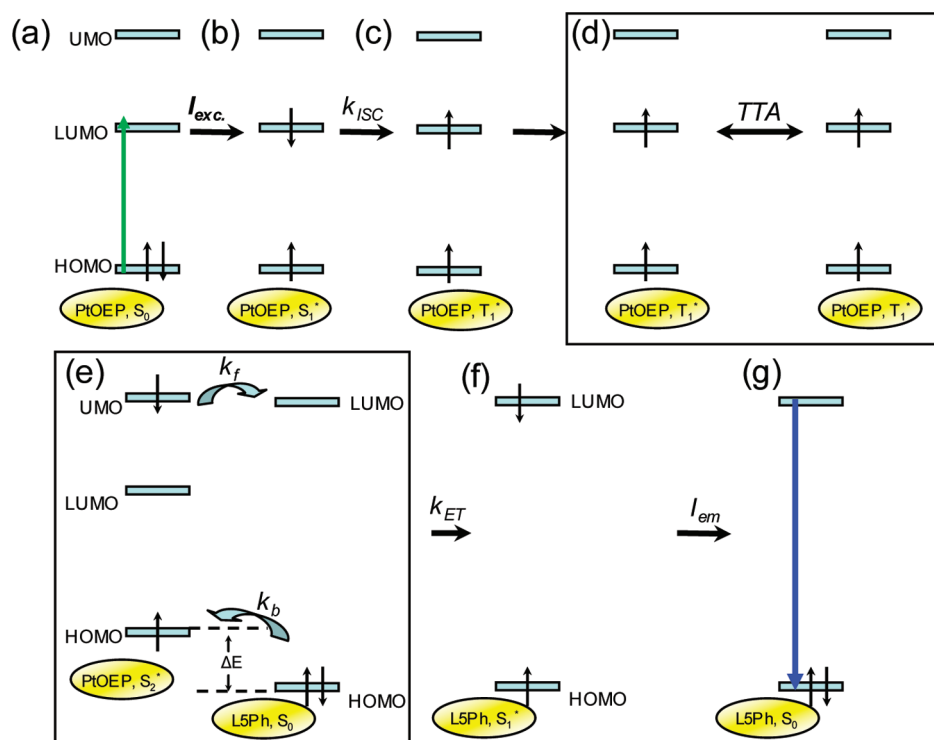
Figure 3. Room-temperature time-integrated PL spectra for toluene solutions of PF26/PtOEP (\blacktriangle) and LSPH/PtOEP (\triangle) photoexcited at (a) $\lambda_{\text{exc}} = 390$ nm and (b) $\lambda_{\text{exc}} = 532$ nm. Room-temperature time-resolved luminescence kinetics of PtOEP phosphorescence in the spectral region of 600–650 nm (circles) and polymer matrix up-converted luminescence in the spectral region of 400–450 nm (squares) of (c) a PF26/PtOEP 3 wt % film and (d) a LSPH/PtOEP 3 wt % film. Data in both parts c and d were collected after photoexcitation at 532 nm in a dynamic vacuum of 10^{-5} mbar.

energy migration from PtOEP to PF26 cannot explain the generation of TTA-induced photon up-converted luminescence of PF26. In this stage, we speculate that the different lifetime values of Ph_{PtOEP} in the LSPH/PtOEP and PF26/PtOEP films arise because of differences in the aggregation of PtOEP in the two polymeric matrices. The composition-dependent photophysical study⁹ of PF26/PtOEP thin film has shown that the lifetime of Ph_{PtOEP} decreases at high PtOEP contents because of PtOEP aggregation. Further studies on the morphology of LSPH/PtOEP and PF26/PtOEP films are required to clarify this issue.

Because of unfavorable energetics, triplet migration from the photoexcited PtOEP to the polymeric matrices is impeded. At PtOEP loadings of 3 wt %, the formation of PtOEP domains takes place in the polymer matrix composite; therefore, the process of TTA may occur between photoactivated PtOEP molecules within the domain, resulting in the population of a higher-lying electronic state in PtOEP. It was previously suggested⁹ that electron transfer may take place from this state of PtOEP to isoenergetic unoccupied molecular orbitals (UMOs) of the polymeric activator simultaneously with a back electron transfer between the HOMO levels of the PtOEP and the activator. Scheme 1 visualizes the proposed model. Our hypothesis is further supported by the fact that photoexcited metalated porphyrins may act as reducing agents.²⁹ In the proposed electron-exchange scheme, the efficiency of up-converted luminescence will be determined by the energetic barrier ΔE_{HOMO} (step e in Scheme 1), which will hinder the back electron transfer from the polymer HOMO to the PtOEP HOMO levels. On the basis of the voltammetric data in Table 1, we determine the energy difference between the HOMO levels of

PF26 and PtOEP to be $\Delta E_{\text{HOMO}} = 0.52$ eV, whereas the corresponding energy difference between LSPH and PtOEP is $\Delta E_{\text{HOMO}} = 0.31$ eV. We note that the determined ΔE_{HOMO} energy barriers are larger than the barrier that prevents triplet energy migration from PtOEP to LSPH. However, in contrast with the process of triplet energy migration, the ΔE_{HOMO} barriers are attributed to a back electron transfer process that takes place when the polymer/PtOEP systems are not in equilibrium.

To support further the proposed model, we have performed electric-field-induced PL quenching experiments of the up-converted luminescence in thin films of LSPH/PtOEP and PF26/PtOEP, like previously described.⁷ Figure 4 presents the relative quenching of the up-converted luminescence as a function of the reverse bias for both LSPH/PtOEP and PF26/PtOEP devices. The up-converted PL of LSPH/PtOEP is significantly quenched with respect to the up-converted PL of PF26/PtOEP, further suggesting the existence of an intermediate charge transfer (CT) state that mediates the activation of the up-converted luminescence of LSPH. This CT state should reflect the formation of a geminate pair between the negatively charged LSPH and the positively charged PtOEP. On the basis of the active layer thickness of the LSPH/PtOEP and PF26/PtOEP devices, the intensity of the external electric field is two times lower for the LSPH/PtOEP device than for the PF26/PtOEP device. Given that LSPH and PF26 have comparable exciton binding energies,^{30,31} we suggest that the sensitivity of the up-converted luminescence signal to the electric field is not due to electric-field induced LSPH exciton dissociation but due to the dissociation of the LSPH/PtOEP geminate pairs formed after the electron

Scheme 1. Proposed Mechanism for the Generation of TTA Assisted Delayed up-Converted Luminescence in the L5Ph/PtOEP Solid Films^a

^a Excitation of PtOEP molecules at 532 nm (a) results in the formation of the S₁* state of PtOEP (b). The T₁* state of PtOEP is subsequently populated via intersystem crossing [k_{ISC} , (c)]. Following step (c), two T₁* states of adjacent PtOEP molecules interact via TTA. The process of triplet fusion promotes one of the PtOEP molecules to the higher lying electronic state S₂* (d), from where it undergoes an energy transfer reaction with L5Ph via electron-exchange (e). The energy transfer reaction rate k_{ET} depends on the energetic barrier ΔE between the HOMO levels of PtOEP and L5Ph. Following the transfer of energy from PtOEP to L5Ph, the S₁* state of L5Ph is formed (f), and the characteristic delayed up-converted luminescence of L5Ph is observed (g). The terms k_f and k_b correspond to the forward and backward electron transfer steps between the excited PtOEP and the ground state of L5Ph in step (e).

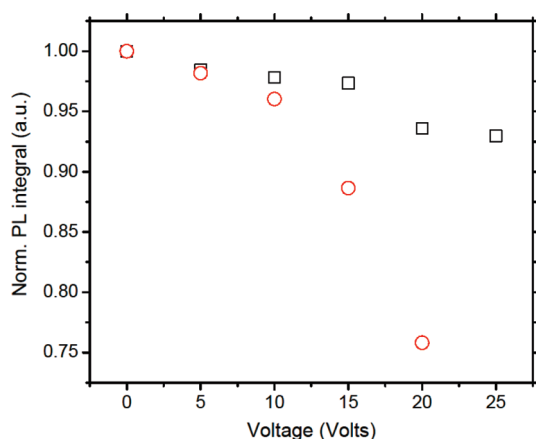


Figure 4. Spectrally integrated up-converted luminescence of the PF26/PtOEP (□) and L5Ph/PtOEP (○) devices as a function of reverse bias. Device structure was glass/ITO/SiO_x/PtOEP blend/SiO_x/Al.

transfer step from PtOEP to L5Ph. In respect to PF26, the stronger quenching of the up-converted L5Ph luminescence suggests that the binding energy of the L5Ph/PtOEP geminate pair is lower than that of PF26:PtOEP. This can be understood as the result of a longer distance between the geminate charges of

the pair. In this stage, we can not provide evidence in support of this explanation; however, the reduced Φ_{PtOEP} lifetime values found in L5Ph/PtOEP indicate enhanced PtOEP aggregation in the system. In this case, the presence of relatively larger domains of PtOEP in the L5Ph matrix could justify a larger Coulomb radius of the L5Ph/PtOEP geminate pair.

In conclusion, we have studied the process of photon energy up-conversion in two different systems consisting of the PtOEP sensitizer mixed with the polymeric activators of either PF26 or L5Ph. For both PF26/PtOEP and L5Ph/PtOEP systems, the triplet energy of the activator lies higher than the triplet energy of PtOEP; therefore, triplet energy migration from the triplet manifold of the photoexcited PtOEP to the polymers is excluded. After the selective photoexcitation of PtOEP in the systems, triplet–triplet annihilation takes place between PtOEP molecules, and a higher-excited state of PtOEP is populated, leading to up-converted luminescence of the activators. The up-converted luminescence was observed both in solution and in the solid state, and it was found to be more efficient for the L5Ph/PtOEP system. In the solid state, the phosphorescence lifetime of PtOEP was found to be much shorter in L5Ph/PtOEP than PF26/PtOEP, suggesting enhanced PtOEP aggregation in the L5Ph matrix. A mechanism for the TTA-induced energy transfer between photoexcited PtOEP and the polymer activators is proposed that operates via an electron-exchange step between PtOEP and polymer hosts. We suggest that TTA between

photoexcited PtOEP molecules results in an electron transfer from PtOEP to the polymer activators and in an electron transfer from the HOMO of the polymer to the single occupied HOMO of the PtOEP. In the suggested scheme, the efficiency of the charge-exchange process depends on the energetic difference between the HOMO levels of activator and PtOEP. We found that for the system that exhibits the most efficient up-conversion (LSPH/PtOEP), the ΔE_{HOMO} value is the lowest. Moreover, for the same system, quenching of the up-converted luminescence is observed by the application of an externally applied electric field.

Our findings suggest the participation of an intermediate state with a charge-transfer character in the excited-state pathway that leads to the generation of up-converted luminescence. The electric-field-induced PL quenching of the up-converted luminescence suggests that the electron exchange between the photoexcited PtOEP and LSPH takes place in a sequential and not a concerted manner. Transient absorption spectroscopy experiments could possibly further clarify this subject by the identification of charge species in the nanosecond to microsecond time regime after the occurrence of the TTA reaction within the PtOEP domains of the up-converting composites.

EXPERIMENTAL SECTION

Electrochemistry was performed with a typical three electrode cell using an autolab PGSTAT 301 (Echochemie, Utrecht, The Netherlands) with a 1 mm diameter Au disk electrode (BAS, West Lafayette, IN), a coiled Pt wire counter electrode and a tetrabutylammonium tetrafluoroborate (0.1 M) Ag/Ag^+ was used as the quasireference electrode (QRE). Both the used polyelectrolyte and the solvent were of high purity in the order of 99 and 98.8%, respectively. All measurements were performed directly after purging of N_2 throughout the prepared solutions to avoid unwanted electrochemical interaction of the measured species with dissolved O_2 . CV sweeps were recorded at 100 mV/s, and DPV was performed at an interval of 100 ms with modulation of 20 ms at 15 mV with data recorded in 1 mV increments. The error in the determination of the $E_{1/2}$ was ± 0.02 V.

For the fabrication of the PF26/PtOEP and LSPH/PtOEP devices, ITO substrates were used as the hole-collecting electrodes, and the deposition of the photoactive layers on the substrate took place after the evaporation of 20 nm thick layer SiO_x on ITO. Subsequently, the polymer/PtOEP blend layers were spin-coated onto the ITO/ SiO_x substrates, and a 20 nm thick layer of SiO_x was evaporated on top. Finally, an aluminum (Al) layer was deposited by thermal evaporation and served as the electron-collecting electrode. The obtained films of PF26/PtOEP and LSPH/PtOEP had nominal thickness of 100 and 200 nm, respectively. For each system, the up-converted luminescence was recorded as a function of the reverse bias applied on the corresponding device.⁷

ASSOCIATED CONTENT

S Supporting Information. UV–vis absorption spectra of the PF26 and LSPH polymers in toluene and PF26/PtOEP and LSPH/PtOEP toluene solutions. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ACKNOWLEDGMENT

P.E.K. thanks the Marie Curie Training Site HPMT-CT-2000-00015 and the European CO.DE. Research Training Network HPRN-CT-2000-00003 for providing financial support. F.L. thanks the Fonds der Chemischen Industrie for a Kekulé scholarship. The identification of commercial materials and their sources is given in describing the experimental results. In no case does this identification imply recommendation by the National Institute of Standards and Technology, nor does it imply that the material is the best available.

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