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Examining the role of acceptor molecule structure in self-assembled bilayers: surface loading, stability, energy transfer, and upconverted emission†

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Self-assembly of sensitizer and acceptor molecules has recently emerged as a promising strategy to facilitate and harness photon upconversion via triplet–triplet annihilation (TTA-UC). In addition to the energetic requirements, the structure and relative orientation of these molecules can have a strong influence on TTA-UC rates and efficiency. Here we report the synthesis of five different acceptor molecules composed of an anthracene core functionalized with 9,10- or 2,6-phenyl, methyl, or directly bound phosphonic acid groups and their incorporation into self-assembled bilayers on a ZrO₂ surface. All five films facilitate green-to-blue photon upconversion with Φ_{uc} as high as 0.0023. The efficiency of TTA, and not triplet energy transfer, fluorescence, or losses via FRET, was primarily responsible for dictating the Φ_{uc} emission. Even for molecules having similar photophysical properties, variation in the position of the phosphonic acid resulted in dramatically different Φ_{TTA} , I_{th} values, γ_{TTA} , and D . Interestingly, we observed a strong linear correlation between Φ_{TTA} and the I_{th} value but the cause of this relationship, if any, is unclear.

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1. Introduction

Photon upconversion *via* triplet–triplet annihilation (TTA-UC), wherein two low energy photons are combined to generate a higher energy excited state, is of interest for a number of applications including bioimaging,^{1,2} oxygen sensing,² photocatalysis,³ and solar energy conversion.^{4–11} Regarding the latter, TTA-UC is particularly intriguing since it provides a means of surpassing the Shockly–Queisser limit ($\sim 33\%$)¹² and increase maximum theoretical solar cell efficiencies to upwards of 43% under AM 1.5 solar irradiation.^{9,13,14}

During TTA-UC, a sensitizer molecule (**S**) absorbs a low energy photon, then undergoes intersystem crossing followed by triplet energy transfer to an acceptor (*a.k.a.* an annihilator or emitter) molecule (**A**). When two **A** triplet excited states are in proximity they can undergo TTA where emission from the resulting singlet excited state is hypsochromically shifted relative to the excitation light and thus the photon energy is upconverted during the process.

A majority of TTA-UC research has been performed with sensitizer and acceptor molecules suspended in solution or

a rubbery polymer matrix.^{15–21} Through this effort, a great deal has been learned about how the thermodynamics of the molecules suspended in a medium can influence TTA-UC. For example, subtle variations in the structure of the prototypical anthracene acceptor molecule²² can have a large impact on the triplet excited state lifetime, singlet/triplet potential energy surface, and ultimately the TTA-UC yield.^{23–25}

Building upon these host-based UC schemes, recently there has been a sharp increase in using supramolecular assemblies^{26,27} like micelles/lipid membranes,²⁸ polymers/dendrimers,^{29,30} host–guest interactions,³¹ ionic crystals,³² and MOFs^{33,34} to facilitate TTA-UC. Of the assembly strategies, binding **S** and **A** molecules on nanocrystalline metal oxide surfaces (TiO₂ or ZrO₂) has emerged as a means of not only facilitating UC emission,^{10,35–38} but also extracting charge from the upconverted state and directly harnessing TTA-UC in a solar cell.^{5,6,10,33,39,40} Self-assembled bilayers (Fig. 1) are particularly promising in that under solar flux, TTA-UC photocurrents of $>0.1 \text{ mA cm}^{-2}$ have been achieved which is above the device relevance threshold proposed by Schmidt and coworkers.⁴¹

The bilayer films are prepared by stepwise soaking⁴² of a metal oxide film in a solution of **A**, then linking metal ions, and finally **S**.³⁹ Unlike in a solvent or host matrix, where molecules are relatively free to rotate and collide, these assembled systems geometrically restrict the mobility and orientation of the **S** and **A** molecules. Thus, in addition to the energetic influence noted

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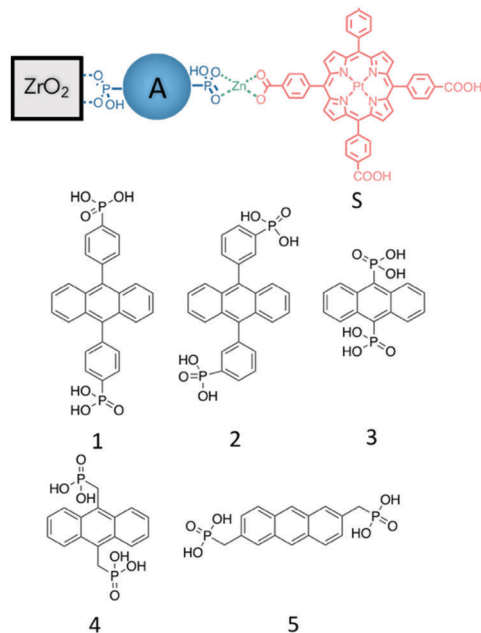


Fig. 1 Schematic representation of the self-assembled bilayer on ZrO_2 and structures for Pt(II)-tetrakis(4-carboxyphenyl)porphyrin (**S**) and acceptor molecules (**1**–**5**).

above, presumably structural variations that tune the inter-molecular distance and orientation are critical in dictating TTA-UC rates and efficiencies.

Recently, our group reported that for two energetically similar diphenylanthracene molecules (**1** and **2** in Fig. 1), changing the phosphonate metal ion binding group from the *para*- to the *meta*-position results in a 3-fold decrease in the TTA-UC emission quantum yield.¹¹ In an effort to further elucidate the role of the acceptor structure on TTA-UC in bilayer films, here we report the synthesis of three new anthracene dyes substituted at the 9,10- or 2,6-positions with phosphonate metal ion binding groups (Fig. 1). The photophysical properties of dyes **1**–**5** in solution, on films and combined with Pt(II)-tetrakis(4-carboxyphenyl)porphyrin (**S**) sensitizer in the bilayer film are described.

2. Experimental section

2.1 Materials

1,4-Dibromobenzene, 1,3-dibromobenzene, anthraquinone, *n*-butyl lithium, nickel bromide, triethylphosphite, trimethylsilyl bromide, toluene, benzene, benzyl alcohol, *N,N*-dimethylformamide, aluminium chloride, chromium(VI) oxide, copper(II) sulfate, zinc powder, potassium carbonate, *N*-bromosuccinimide, 9,10-dibromoanthracene, acetic anhydride, 95% sulfuric acid, glacial acetic acid, hydrochloric acid, ammonium hydroxide solution, bis(dichloromethyl)anthracene, iodomethane, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone, phosphorus tribromide, lithium aluminium hydride, zinc acetate dihydrate, and Pt(II) *meso*-tetra(4-carboxyphenyl)porphine (Frontier Scientific), were purchased from their respective suppliers, in parentheses, and used as received.

All other reagents and solvents (analytical reagent grade) have been purchased and used without further purification from Alfa Aesar. Tetrahydrofuran and dichloro-methane used in synthesis have been dried and degassed prior to use. Glass substrates were purchased from Hartford Glass Co. Meltonix film (1170-25) and a Vac'n Fill Syringe (65209) were purchased from Solaronix. Micro glass cover slides (18 × 18 mm) were obtained from VWR. ZrO_2 sol-gel paste and nanocrystalline films were prepared following previously reported procedures.^{43–45}

2.2 Sample preparation – device fabrication

Spectroscopic samples were prepared in a sandwich cell-type architecture.^{5,6,11,39,40,46} Briefly, glass was cut into 2.2×2.2 cm pieces, and an active area of 1 cm^2 metal oxide was prepared by doctor blading ZrO_2 (1 layer of Scotch tape) and sintering. Dyes were then loaded onto the metal oxide, as described below. A small hole ($d = 1.1$ mm) was drilled into the corner of the 2.2×2.2 cm glass slide. A 2 mm wide 2.2×2.2 cm Meltonix film was placed between the two glass slides, and the entire ensemble was heated to $\sim 150^\circ\text{C}$ for 7 s using a home-built heating/sealing apparatus described previously.⁴⁷ The cells were then transferred to a glovebox (a VTI Universal purified glovebox, N_2 atmosphere) where dry and oxygen-free acetonitrile was injected using a Vac'n Fill Syringe through the 1 mm hole to fill the interior of the cells. A meltonix film and small piece of a micro glass cover slide were then heated to seal the hole used for solvent injection.

2.3 Sample preparation – film formation

Photophysical cells were prepared following our previously published procedure with minor modification.^{5,6,11,39,40,46} Adsorption isotherms of the **A** molecules on ZrO_2 were measured by immersing thin films in 3 mL of DMSO solutions of **1**–**5** with concentrations of 25, 50, 70, 100, 200, 300, 400 and 500 μM . The slides were removed, rinsed with methanol, and dried under a stream of air. More details will be seen in the results and discussion section.

2.4 Surface area measurement

The surface area of the ZrO_2 nanocrystalline film was determined from nitrogen adsorption-desorption isotherms at 77 K (Quantachrome Corporation, Autosorb iQ.). The surface area was determined using the BET equation.⁴⁸ The samples were degassed under vacuum (5×10^{-3} mmHg) at 120°C for 4 h, prior to measurement, to evacuate physisorbed moisture. The surface area was calculated to be $113.6 \text{ m}^2 \text{ g}^{-1}$. 4 strips of $10 \text{ cm} \times 1.5 \text{ cm}$ ZrO_2 film were scraped off the glass and dried in an oven overnight. It yielded 30.1 mg, which further gives the surface area ($A_{1 \times 1}$) of a $1 \text{ cm} \times 1 \text{ cm}$ area of film as 565 cm^2 .

2.5 Photostability measurements

The light from a blue (375 nm, fwhm ~ 30 nm, 1.53 mW cm^{-2}) mounted high power LED (Thorlabs, Inc., M455L2) powered by a T-Cube LED driver (Thorlabs, Inc., LEDD1B) was used. The light output was directed onto the derivatized thin films placed at 45° in a standard 10 mm path length cuvette containing 3 mL of MeCN. The illumination spot was adjusted to coincide both with the thin films and the perpendicular beam path of a Varian Cary 50 UV-vis

spectrophotometer. The absorption spectrum (360–800 nm) of the film was obtained every 10 s for 11 600 s (decreased by 5% after the first 4000 s of measurement). The incident light intensity was measured using a thermopile detector (a Newport Corp 1918-C meter and a 818P-020-12 detector). The solution temperature, 22 ± 2 °C, was consistent throughout the duration of the experiment.

2.6 Absorption measurements

Absorption spectra were recorded using an Agilent 8453 UV-visible photo diode array spectrophotometer. Extinction coefficients for **A** in DMSO were determined from the absorption spectra of solutions with a known concentration of dye in a 1×1 cm quartz cuvette. Thin film absorption spectra were obtained by placing dry, derivatized ZrO_2 slides perpendicular to the detection beam path.

2.7 Steady-state emission

An Edinburgh FLS980 fluorescence spectrometer was used to collect emission data at room temperature. A housed 450 W Xe lamp/single grating (1800 λ/mm , 250 nm blaze) Czerny–Turner monochromator or a Nd:YAG laser (Aixiz, AD-532-400T) was used as an output to excite the samples. The Nd:YAG laser was passed through a variable neutral density filter (Edinburgh F-B01 laser mount), a 2 mm diameter iris (Newport ID-1.0) and then directed to the sample *via* a flip mirror. Emission from the sample was passed through a 532 nm notch filter (Thorlabs Inc., NF533-17), the single grating (1800 λ/mm , 500 nm blaze) Czerny–Turner monochromator and then detected by a Peltier-cooled Hamamatsu R928 photomultiplier tube. A power meter (Ophir Vega 7Z01560) with a high sensitivity power sensor (Ophir 3A-FS 7Z02628) was used to measure laser intensities. Fluorescence quantum yields of **A** in DMSO are estimated relative to DPA in EtOH

($\Phi_F = 95\%$)⁴⁹ by $\Phi_A = \Phi_{\text{DPA}} \frac{I_A A_{\text{DPA}} n_A^2}{I_{\text{DPA}} A_A n_{\text{DPA}}^2}$,³⁹ where I_A and I_{DPA} are

the integrated emission intensities of **A** in DMSO and DPA in EtOH (from 380–550 nm) under excitation at 360 nm, respectively. A_A and A_{DPA} are their respective absorbances at 360 nm. 1.36⁵⁰ and 1.47⁵¹ are used for the refractive indices of n_A and n_{DPA} . Emission quantum yields for upconverted emission from $\text{ZrO}_2\text{-A-Zn-S}$ (**A** = 2–5) are estimated relative to $\text{ZrO}_2\text{-1-Zn-S}$ using equation $\Phi_{\text{UC}} = \Phi_{\text{UC1}} \frac{I_{\text{UC}} A_{\text{UC1}} n_{\text{UC}}^2}{I_{\text{UC1}} A_{\text{UC}} n_{\text{UC1}}^2}$ where I_{UC} and I_{UC1} are the integrated emission intensities of $\text{ZrO}_2\text{-1-Zn-S}$ and $\text{ZrO}_2\text{-A-Zn-S}$, respectively. A_{UC} and A_{UC1} are their respective absorbances at 532 nm. Given the similar cell architecture, composed of glass, ZrO_2 and MeCN, the refractive indices (n_{UC} and n_{UC1}) are assumed to be the same for both samples. The emission intensities were acquired with 532 nm excitation (2.5 W cm^{-2}) using the sandwich cell architecture placed at an ~ 45 degree angle relative to the incident excitation. Emission, perpendicular to the incident laser, was passed through a 532 nm notch filter (Thorlabs Inc., NF533-17) before entering the monochromator/detector.

2.8 Time-resolved emission

Emission decay kinetics, not including TTA-UC emission, were collected at room temperature using an Edinburgh FLS980

fluorescence spectrometer. The emission decay traces were acquired using either time-correlated single-photon counting (TCSPC; 1024 channels; a 200 ns window) with data collection for 10 000 counts or multichannel scaling (MCS) acquisition mode with 532 nm excitation from a 60 W microsecond flashlamp (pulse width $< 2.5 \mu\text{s}$) at a 100 Hz repetition rate for lifetime measurements of **A** and PtP, respectively. TCSPC excitation was provided by an Edinburgh EPL-360 ps pulsed light emitting diode (360 ± 10 nm, pulse width 892 ps) operated at 10 MHz. Emission was passed through a single grating (1800 λ/mm , 500 nm blaze) Czerny–Turner monochromator and detected by a Peltier-cooled Hamamatsu R928 photo-multiplier tube. Emission decay kinetics for the films were fitted with a biexponential function $y = A_1 e^{-k_1 x} + A_2 e^{-k_2 x} + y_0$ using the Edinburgh software package, and a weighted average lifetime calculated using $\langle \tau \rangle = \sum A_i \tau_i^2 / \sum A_i \tau_i$.

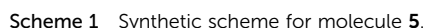
TTA-UC emission decays for **A** and **PtP** in DMSO used to determine τ_A ³ were collected using an Edinburgh Instruments LP980-KS laser flash photolysis spectrometer. Measurements were carried out using sealed 1×1 cm quartz cuvettes containing oxygen free DMSO solutions. The spectrometer is composed of a Continuum Surelite EX Nd:YAG laser combined with a Continuum Horizon OPO (532 nm, 5–7 ns, operated at 1 Hz, beam diameter ~ 0.5 cm, 2.5–5 mJ per pulse) integrated into the Edinburgh LP980 spectrometer. For time-resolved scans, the emission was passed through a TMS302-A monochromator (1800 grooves per mm grating) with a 300 mm focal length in the Czerny Turner configuration and detected by a Hamamatsu R928 photomultiplier tube. Edinburgh's L900 (version 8.2.3, build 0) software package was used to process detector outputs. As with emission, the decay kinetics were fit using a biexponential function, and the results are presented as a weighted average lifetime.

3. Result and discussion

3.1 Acceptor design and synthesis

Acceptor molecules 4,4'-(anthracene-9,10-diyl)bis(4,1-phenylene)diphosphonic acid (**1**),³⁹ and 4,4'-(anthracene-9,10-diyl)bis(3,1-phenylene)diphosphonic acid (**2**)¹¹ were prepared by following previously published procedures. Anthracene-9,10-diphosphonic acid (**3**)⁵² and anthracene-9,10-diylbis(methylene)diphosphonic acid (**4**)⁵³ were prepared by first generating the ethyl ester compounds from 9,10-dibromo anthracene and 9,10-bis(dichloromethyl)anthracene, respectively, using variations of the Arbuzov reaction,⁵⁴ followed by ester group cleavage using TMS-Br.

The multistep synthesis of 2,6-anthracenediylbis(methylene)-bisphosphonic acid (**5**) is shown in Scheme 1. Briefly, 2,6-dimethylanthracene (**5a**) was prepared from benzyl alcohol following the procedure of Cao *et al.*⁵⁵ Initially we attempted to generate 2,6-bis(bromomethyl)anthracene (**5d**) using *N*-bromosuccinimide (NBS) following a previously published procedure.⁵⁶ However, bromination of the methyl substituents was unsuccessful presumably due to the higher reactivity of the 9 and 10 positions of the anthracene core.^{57,58} Instead the product was synthesized by



3.2 Solution photophysics

3.3 ZrO₂-A film formation, photophysics, and photostability

The bilayer films were prepared using a step-wise soaking procedure first implemented by Mallouk, Haga, and others on planar surfaces^{45,60,61} and then later extended to mesoporous substrates.⁴² Briefly, nanocrystalline ZrO_2 is first soaked in a DMSO solution of **A** for 12 hours, then Zn^{II} , and finally a

Table 1 Photophysical properties of **1–5** in DMSO

	λ_{abs} (nm) ($\varepsilon, \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$)	λ_{em}^a (nm)	$\tau_{\text{S1}}^{a,b}$ (ns)	Φ_{FL}^a	k_{r}^c (s^{-1})	k_{nr}^d (s^{-1})
1	358(0.77), 376(1.29), 397(1.22)	419, 433	5.9	0.93	1.6×10^8	1.2×10^7
2	358(0.72), 376(1.16), 397(1.10)	414, 433	6.1	0.92	1.5×10^8	1.3×10^7
3	371(0.54), 388(0.68), 410(0.60)	428, 446	10.9	0.79	7.3×10^7	1.9×10^7
4	365(0.64), 385(1.10), 407(1.09)	413, 436, 462	10.1	0.85	8.4×10^7	1.5×10^7
5	348(0.36), 366(0.47), 385(0.36)	429, 444, 459	5.2	0.14	2.7×10^7	1.7×10^8

^a $\lambda_{\text{ex}} = 360 \text{ nm}$. ^b From an exponential fit to the excited state decay at the emission maximum. ^c $k_r = \Phi_{\text{EL}}/\tau_{\text{S1}}$. ^d $k_{\text{nr}} = (1 - \Phi_{\text{EL}})/\tau_{\text{S1}}$.

DMSO solution of **S**.³⁹ Each step of the surface modification procedure was monitored by UV-vis or attenuated total reflectance infrared (ATR-IR) spectroscopy. ZrO₂ was chosen as the substrate for this work because of its relatively high conduction band potential which inhibits excited state electron transfer from the dyes to the metal oxide surface and thus emission can be observed without concerns of quenching by the substrate.^{62,63}

The binding of **1–5** to ZrO₂ obeys Langmuir isotherm behavior⁶⁴ with the maximum surface coverage ($\Gamma_{\max}$) and the surface adsorption constant (K_{ad}) reported in Table 2. Surface coverages (Γ in mol cm⁻²) are estimated with the expression $\Gamma = (A(\lambda)/\varepsilon(\lambda))/1000$, where $A(\lambda)$ is the maximum absorbance of each molecule on the slides and ε is the molecular molar extinction coefficient for the dyes in DMSO.⁶⁵ From the isotherms (Fig. S2, ESI†), it was determined that a 250 μM solution of **1** and 300 μM solutions of **2–5** were sufficient to achieve high surface loadings ($\sim 1 \times 10^{-8}$ mol cm⁻²) and were used for all measurements reported below.

Because the $\Gamma_{\max}$ values are only a relative estimate of surface coverage and are film thickness dependent, we sought to determine the center-to-center distance between **A** molecules ($d_{\text{A-A}}$) and the results are summarized in Table 2. These values were determined by first quantifying the surface area of ZrO₂ using BET isotherm measurements with N₂ as the adsorbent. The dye molecules were then loaded on the surface under full coverage conditions, desorbed by soaking the films in a 0.1 M KOH solution, and the amount of loaded dye was calculated from the absorption intensity of the solution using Beer's law (see ESI† for more details). The $d_{\text{A-A}}$ values were then calculated from the surface area and total number of dye molecules assuming hexagonal packing of spherical molecules. $d_{\text{A-A}}$ for **1**, **2**, **4**, and **5** were similar, ranging from 9–11 Å. Compound **3** exhibited the largest intermolecular spacing at 16 Å. Given the similarity in size of these molecules it is not entirely clear to us why **3** would exhibit a lower surface coverage and larger intermolecular distance. Regardless, all intermolecular spacings are sufficiently close such that intermolecular Dexter energy transfer⁶⁶ and TTA can occur.^{67,68}

The absorption and emission spectra for **1–5** bound to ZrO₂ (herein referred to as ZrO₂-**A**) are shown in Fig. 3a and b, respectively. The dyes on ZrO₂ exhibit similar absorption energies and spectral features as in solution (Fig. 3a). Upon excitation at 360 nm, blue emission is observed from all ZrO₂-**A** films (Fig. 3b) with similar but broadened emission features when compared to in solution.

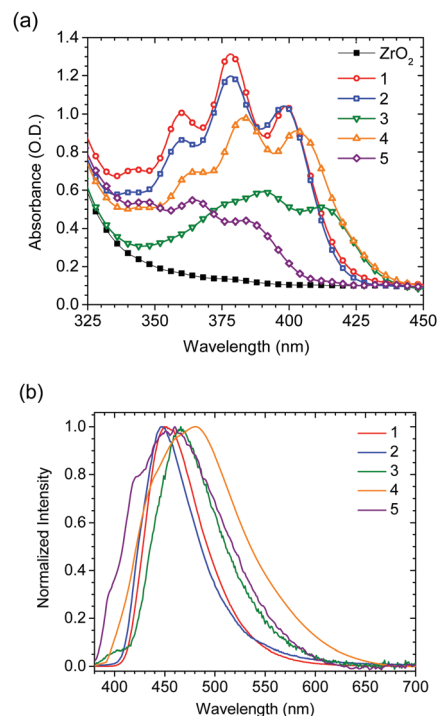


Fig. 3 (a) Absorption spectra in air and (b) emission spectra in acetonitrile for **1–5** on ZrO₂. (λ_{ex} = 360 nm.)

The photostability of acceptor molecules is critical to maintaining high TTA-UC efficiencies for long term applications. This is a particular concern with anthracene molecules since they are known to undergo dimerization and decomposition.^{69,70} With this in mind, the photostabilities of ZrO₂-**A** films in MeCN were investigated following a previously published procedure⁷¹ by monitoring changes in the absorbance spectra of the films under continuous 365 nm irradiation (1.5 mW cm⁻²). The results for ZrO₂-**1** can be seen in Fig. 4a with the remaining spectra in the ESI†. For the films of **1–5** there is a uniform decrease in the absorption intensity at all wavelengths. There was no absorption from the external solution after irradiation and color did not return after heating the films to 80 °C overnight indicating that the spectral changes are due to dye decomposition and not desorption or photo-dimerization of **A**.⁶⁹ Under similar conditions but using deaerated MeCN, the decomposition is slowed by several orders of magnitude (Fig. S4, ESI†). Given their sensitivity to the atmosphere, the photoinduced dye decomposition is presumably due to the well known [4+2]

Table 2 Surface loading and photophysical properties of ZrO₂-**A**

	$\Gamma_{\max}^a$ (mol cm ⁻²)	$d_{\text{A-A}}^b$ (Å)	λ_{abs}^c (nm)	λ_{em}^d (nm)	$\tau_{\text{S1}}^{d,e}$ (ns)	K_{ad}^f (mmol ⁻¹)	τ_{dec}^g (s)	k_{dec}^h (s ⁻¹)
1	1.0×10^{-7}	8.6	360, 378, 399	458	7.6	0.016	420	0.0027
2	9.8×10^{-8}	9.7	360, 378, 398	447	6.6	0.012	400	0.0026
3	7.8×10^{-8}	16.0	391, 412	466	2.6	0.019	1000	0.0011
4	9.6×10^{-8}	11.2	365, 383, 403	471	6.8	0.020	310	0.0032
5	9.9×10^{-8}	8.9	346, 364, 383	464	11.1	0.018	290	0.0044

^a Calculated using $\Gamma = (A(\lambda)/\varepsilon(\lambda))/1000$. ^b Calculated from the ZrO₂ surface area and total dye loading. ^c Measured in DMSO. ^d λ_{ex} = 360 nm. ^e Weighted average lifetime from the biexponential fit. ^f Calculated using the Langmuir equation: ($\Gamma = \Gamma_{\max}((K_{\text{ad}}[\text{A}])/(1 + K_{\text{ad}}[\text{A}]))$). ^g Weighted average lifetime from the biexponential fit of Fig. 4b. ^h $k_{\text{dec}} = \tau_{\text{dec}}^{-1}$.

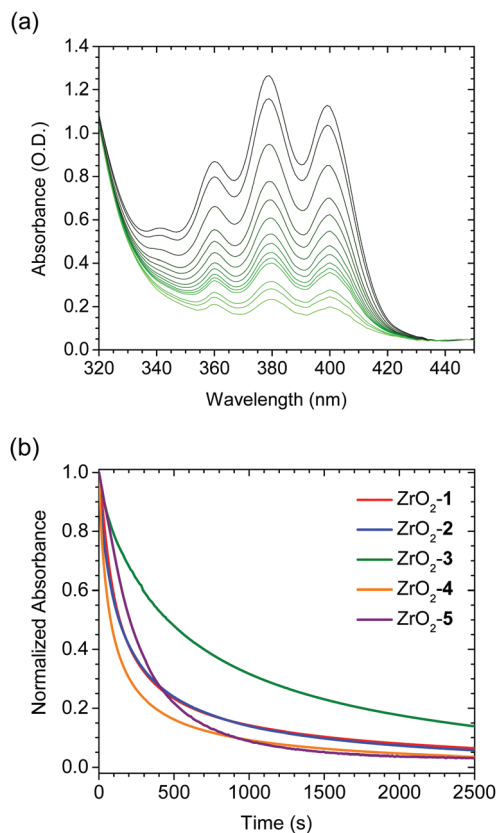


Fig. 4 Changes in the absorption spectrum of (a) $\text{ZrO}_2\text{-1}$ in MeCN under constant 365 nm (1.5 mW cm^{-2}) irradiation from 0 (black) to 2 hours (green) and (b) the normalized absorbance intensity versus time for **1–5** on ZrO_2 in MeCN.

cycloaddition of singlet oxygen across the 9,10-positions of anthracene.⁷⁰

The time-dependent changes in absorption were fit with the biexponential function and are presented as an average decomposition rate constant (k_{dec}) calculated as the inverse of the weighted-average lifetime ($k_{\text{dec}} = \langle \tau \rangle^{-1}$), and the results are summarized in Table 2. The spectral change and desorption rate constant were reproducible within $\pm 10\%$ across two independently prepared samples.

Of the films, $\text{ZrO}_2\text{-4}$ and $\text{ZrO}_2\text{-5}$ were the least stable decomposing with a rate constant greater than $3 \times 10^3 \text{ s}^{-1}$. Slightly more stable ($k_{\text{dec}} = 2.6 \times 10^3 \text{ s}^{-1}$) were diphenyl substituted compound **1** and **2**. Phenyl substituents are known to decrease reactivity at the 9,10-positions due to increased steric hindrance.⁷² Interestingly, compound **3** was the most stable of the series which may be due to similar steric hindrance and/or a change in reactivity at the 9,10 position due to the phosphonate groups.

3.4 $\text{ZrO}_2\text{-A-Zn-S}$ film formation

Zn^{II} was chosen as the metal linking ion for bilayer film formation because it is photophysically and electrochemically inert under the measurement conditions applied here.⁷³ Zn^{II} coordination to the non-surface bound phosphonate groups of

A was achieved by soaking the $\text{ZrO}_2\text{-A}$ films in a solution of $400 \mu\text{M Zn}(\text{CH}_3\text{COO})_2$ in methanol for 30 minutes.^{5,39,40,46} Metal ion coordination was monitored using ATR-IR spectroscopy and the results are shown in ESI†. All $\text{ZrO}_2\text{-A}$ films exhibit a peak at $\sim 950 \text{ cm}^{-1}$ that is indicative of O–P–O bending of the non-surface bound PO_3H_2 group.⁷⁴ Upon soaking $\text{ZrO}_2\text{-A}$, the $\sim 950 \text{ cm}^{-1}$ peak disappears with concomitant growth of features at 1000 to 1150 cm^{-1} consistent with metal ion coordination to the PO_3H_2 groups of **1–5**.⁷⁵

The bilayer film ($\text{ZrO}_2\text{-A-Zn-S}$) was then prepared by submerging $\text{ZrO}_2\text{-A-Zn}$ in a $100 \mu\text{M}$ solution of **S** in DMSO. The soaking time for each film (see ESI† for treatment times) was varied to generate films with an **A** to **S** ratio of 10 to 1 which was previously reported to minimize “self-filtering” losses and maximize TTA-UC emission from bilayer films.³⁹ Upon soaking $\text{ZrO}_2\text{-A}$ in a solution of **S**, without $\text{Zn}(\text{CH}_3\text{COO})_2$ treatment, there was minimal absorption contribution from the porphyrin molecule (Fig. S6, ESI†). This observation indicates that the surface coverage of **A** is sufficiently high to inhibit the sensitizer from binding directly to the ZrO_2 surface.

While we do not have direct structural information about the interface, the necessity of Zn^{II} linking ions for **S** loading supports the formation of a bilayer architecture similar to that depicted in Fig. 1 and not a co-deposited film. The lack of structural data also brings into question the dynamic motion of the molecules on the surface which would influence the energy transfer and TTA dynamics. Previously published neutron scattering experiments⁷⁶ and theoretical modelling⁷⁷ of molecular monolayers on metal oxide surfaces indicate that at high surface loadings, the molecular rotation and cross-surface mobility are significantly limited by steric hindrance due to tight inter-molecular packing. Presumably this molecular motion is further hindered in the bilayer film because of the layered structure but further structural characterization is necessary to test this hypothesis.

3.4.1 $\text{ZrO}_2\text{-A-Zn-S}$ TTA-UC emission. Samples for emission measurements were prepared in a glove box under a N_2 atmosphere following a previously published procedure.³⁹ Upon 532 nm excitation (3 W cm^{-2}) all of the $\text{ZrO}_2\text{-A-Zn-S}$ films exhibit a blue emission feature from 420–500 nm (Fig. 5) that resembles

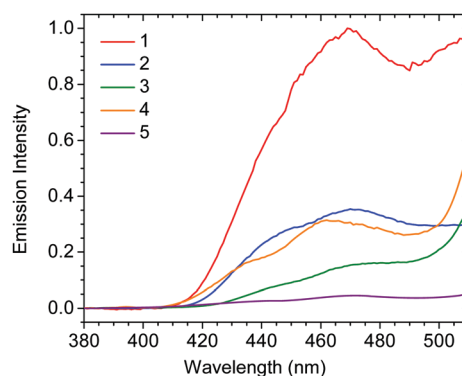


Fig. 5 Emission spectra for $\text{ZrO}_2\text{-A-Zn-S}$ in deaerated MeCN where **A** = **1–5** ($\lambda_{\text{ex}} = 532 \text{ nm}$, 3 W cm^{-2}).

Table 3 Quantum yields for the TTA-UC processes of $\text{ZrO}_2\text{-A-Zn-S}$ in oxygen free MeCN (**A** = **1-5**)

A	Φ_{uc}^a	Φ_{FL}	k_{TET}^b (s^{-1})	Φ_{TET}^c	J^d ($\text{cm}^3 \text{M}^{-1}$)	k_{FRET}^e (s^{-1})	Φ_{FRET}^f	Φ_{out}^g	Φ_{TTA}^h
1	0.0023	0.93	1.3×10^4	0.33	2.6×10^{-11}	7.75×10^6	0.05	0.95	0.0057
2	0.0008	0.92	1.3×10^4	0.33	2.8×10^{-11}	9.30×10^6	0.06	0.94	0.0020
3	0.0004	0.79	2.1×10^4	0.59	3.3×10^{-11}	2.44×10^8	0.38	0.62	0.0009
4	0.0007	0.85	1.7×10^4	0.52	3.4×10^{-11}	2.37×10^7	0.14	0.86	0.0013
5	0.0001	0.14	1.5×10^4	0.44	2.8×10^{-14}	1.86×10^8	0.58	0.42	0.0027

^a Measured relative to $\text{ZrO}_2\text{-(1)-Zn-S}$ ($\Phi_{\text{uc}} = 0.0023$) via actinometry.³⁹ ^b $k_{\text{TET}} = 1/\tau_{\text{s(bl)}} - 1/\tau_{\text{s}}$. ^c $\Phi_{\text{TET}} = 1 - \tau_{\text{s(bl)}}/\tau_{\text{s}}$. ^d $J = \int_0^\infty F_{\text{A}}(\lambda) \epsilon_{\text{S}}(\lambda) \lambda^4 d\lambda / \int_0^\infty F_{\text{A}}(\lambda) d\lambda$. ^e $k_{\text{FRET}} = 1/\tau_{\text{A(bl)}} - 1/\tau_{\text{A}}$. ^f $\Phi_{\text{FRET}} = 1 - \tau_{\text{A(bl)}}/\tau_{\text{A}}$. ^g $\Phi_{\text{out}} = 1 - \Phi_{\text{FRET}}$. ^h $\Phi_{\text{TTA}} = 2\Phi_{\text{UC}}/\Phi_{\text{ISC}}\Phi_{\text{TET}}\Phi_{\text{FL}}\Phi_{\text{out}}$.

emission from $\text{ZrO}_2\text{-A}$ under direct excitation of **A** at 360 nm. This is in contrast to $\text{ZrO}_2\text{-A}$ and $\text{ZrO}_2\text{-S}$ under 532 nm excitation where no emission was observed in this region due to the lack of absorption and lower energy emission ($\lambda_{\text{em}} = 670$ nm), respectively. The sharp increase in intensity above 500 nm in Fig. 5 can be attributed to scatter from the excitation source.

Upconverted emission quantum yields were measured relative to $\text{ZrO}_2\text{-1-Zn-S}$ ($\Phi_{\text{uc}} = 0.0023$)³⁹ and the results are summarized in Table 3. These measurements were performed under relatively high excitation intensities (3 W cm^{-2}) to ensure that all samples are operating in the maximum efficiency, linear regime (*vide infra*). The highest quantum yield was observed with our prototype bilayer, $\text{ZrO}_2\text{-1-Zn-S}$, and then decreases in the order **2** (0.0008) > **4** (0.0007) > **3** (0.0004) > **5** (0.0001).

The upconverted emission efficiency is equal to the products of the efficiency of each step in the TTA-UC process as shown in eqn (1),⁷⁸

$$\Phi_{\text{UC}} = \frac{\Phi_{\text{ISC}}\Phi_{\text{FL}}\Phi_{\text{TET}}\Phi_{\text{out}}\Phi_{\text{TTA}}}{2} \quad (1)$$

where Φ_{ISC} is the intersystem crossing yield of the sensitizer molecule, Φ_{FL} is the fluorescence quantum yield for **A**, Φ_{TET} is the sensitizer-to-acceptor triplet energy transfer yield, Φ_{out} is the fraction of upconverted states that generate photons that exit the sample and Φ_{TTA} is the efficiency of generating a singlet excited state *via* TTA. The two in the denominator is to account for the two photons in one photon out nature of the TTA-UC process. The measured and calculated quantum yield values for these events in the $\text{ZrO}_2\text{-A-Zn-S}$ films are summarized in Table 3. Φ_{ISC} was not measured directly here but is assumed to be 1.0 as near unity intersystem crossing yields are known for platinum(II)porphyrin molecules.⁷⁸

Sensitizer-to-acceptor triplet energy transfer rates and yields were determined using time-resolved spectroscopy following previous published procedures.⁴⁶ Briefly, the phosphorescent emission lifetime from the sensitizer molecule ($\lambda_{\text{em}} = 670$ nm) was monitored following 532 nm excitation of two different samples, $\text{ZrO}_2\text{-A-Zn-S}$ ($\tau_{\text{s(bl)}}$) and $\text{ZrO}_2\text{-B-Zn-S}$ (τ_{s}). While the former samples exhibit porphyrin-to-anthracene TET, the latter contains terphenyl-4,4''-diylbisphosphonic acid (**B**) which retains the bilayer structure but is a photo- and electrochemically inert structural analogue of the acceptor molecule that does not undergo TET.^{46,79} The triplet energy transfer rate (k_{TET}) and yield (Φ_{TET}) were calculated using eqn (2) and (3)

$$k_{\text{TET}} = \frac{1}{\tau_{\text{s(bl)}}} - \frac{1}{\tau_{\text{s}}} \quad (2)$$

$$\Phi_{\text{TET}} = 1 - \frac{\tau_{\text{s(bl)}}}{\tau_{\text{s}}} \quad (3)$$

and the results are summarized in Table 3.

The rate and efficiency of TET are primarily dictated by the thermodynamic driving-force for electron exchange and the distance between the donor (**S**) and acceptor (**1-4**) molecules.⁶⁶ Of the acceptor molecules, **3** exhibited the fastest ($k_{\text{TET}} = 2.1 \times 10^4 \text{ s}^{-1}$) and most efficient ($\Phi_{\text{TET}} = 0.59$) TET. This high yield is presumably due to the lack of phenyl or methyl groups between the anthracene core and the phosphonate metal ion binding group, effectively decreasing the distance between **S** and **3**. Based on the experimentally determined singlet excited state energies, one could assume that the triplet of **3** is also lower than the other complexes, and thus increases the driving force for TET, however we were unable to quantify the triplet energy by directly observing phosphorescent emission from **3**, or any of the acceptor molecules reported here, even at low temperatures and in the presence of methyl iodide.⁸⁰

Interestingly, **1** and **2** exhibit the same TET rates ($k_{\text{TET}} = 1.3 \times 10^4 \text{ s}^{-1}$) and efficiencies ($\Phi_{\text{TET}} = 0.33$). Given the difference in position of the surface/metal ion binding groups, one would anticipate differences in orientation and/or distance between **S** and **1** or **2** in the bilayer film. However, the similarity in the TET rate/yield suggests that energetics, which are similar for the two molecules, are primarily responsible for dictating TET. Likewise, the methyl phosphonate complexes **4** and **5** exhibit similar TET metrics.

As noted above, Φ_{out} is the fraction of upconverted states that generate photons that exit the sample. That is, photons that are not lost through quenching *via* A-to-S Förster resonance energy transfer (FRET).⁸¹ Similar to the method described above for TET, FRET was quantified by measuring time-resolved emission at 470 nm upon direct excitation of **A** in films with, $\text{ZrO}_2\text{-A-Zn-S}$ ($\tau_{\text{A(bl)}}$), and without, $\text{ZrO}_2\text{-A}$ (τ_{A}), sensitizer which in this case quenches **A** emission. The FRET rate (k_{FRET}) and efficiency (Φ_{FRET}) were calculated using eqn (4) and (5)

$$k_{\text{FRET}} = \frac{1}{\tau_{\text{A(S)}}} - \frac{1}{\tau_{\text{A}}} \quad (4)$$

$$\Phi_{\text{FRET}} = 1 - \frac{\tau_{\text{A(S)}}}{\tau_{\text{A}}} \quad (5)$$

and the results are summarized in Table 3.

The rate of FRET is dictated by the **A** and **S** dipole orientations, the spectral overlap between **A** emission and **S** absorption (J), and the distance between **A** and **S**.^{82,83}

J values were calculated and the result can be seen in Table 3. Compounds **1** and **2** have similar J values of $2.6 \times 10^{-11} \text{ cm}^3 \text{ M}^{-1}$ and $2.8 \times 10^{-11} \text{ cm}^3 \text{ M}^{-1}$, respectively. Again, although we anticipate differences in orientation and distance between the donor and acceptor in ZrO_2 -**1**-Zn-S and ZrO_2 -**2**-Zn-S films, the J values, combined with the similarity in k_{FRET} and Φ_{FRET} , indicate that the differences in structure of these two bilayers play a nominal role in dictating FRET.

In contrast, compound **3** has a similar J value as **4** ($3.3 \times 10^{-11} \text{ cm}^3 \text{ M}^{-1}$ and $3.4 \times 10^{-11} \text{ cm}^3 \text{ M}^{-1}$, respectively), but exhibits an order of magnitude faster FRET ($k_{\text{FRET}} = 2.4 \times 10^8 \text{ s}^{-1}$) and a more than two-fold higher FRET efficiency ($\Phi_{\text{FRET}} = 0.38$). As was used to rationalize differences in TET, the distance between **S** and **3** is presumably decreased relative to the other **A** molecules resulting in an increased rate and efficiency of FRET in ZrO_2 -**3**-Zn-S.

Interestingly, compound **5** exhibits the fastest ($k_{\text{FRET}} = 1.86 \times 10^8 \text{ s}^{-1}$) and most efficient ($\Phi_{\text{FRET}} = 0.58$) FRET despite the three orders of magnitude lower J value ($2.8 \times 10^{-14} \text{ cm}^3 \text{ M}^{-1}$) relative to **1**–**4**. Collectively these results suggest that both structural factors and spectral overlap can play a critical role in dictating energy transfer in the bilayer. Presumably, molecular engineering could be used to maximize TET but minimize losses due to FRET. Unfortunately, we have no direct structural information about the interface. Efforts are currently underway to use DFT and dynamic molecular mechanics simulations to understand the role of the average intermolecular distance and orientation in dictating FRET and TET. Assuming that FRET is the dominant mechanism quenching the singlet excited state of **A**, then Φ_{out} can be calculated using $\Phi_{\text{out}} = 1 - \Phi_{\text{FRET}}$.

Using eqn (1) and the values reported above,⁷⁸ the efficiency of triplet-triplet annihilation (Φ_{TTA}), was calculated and the values are reported in Table 3. Φ_{TTA} decreases in the order **1** (0.0057) > **5** (0.0027) > **2** (0.0020) > **4** (0.0013) > **3** (0.0009). Of the various steps responsible for TTA-UC, these relatively low numbers suggest that Φ_{UC} in the bilayer films are primarily limited by the Φ_{TTA} values.

For ZrO_2 -**1**-Zn-S, despite having the lowest Φ_{TET} , a combination of large Φ_{FL} , Φ_{out} , and Φ_{TTA} results in the highest overall UC yield. In terms of the efficiency of each process, molecules **1** and **2** are comparable except that Φ_{TTA} of **2** ($\Phi_{\text{TTA}} = 0.0020$) is ~ 3 times lower than for **1** ($\Phi_{\text{TTA}} = 0.0057$) which is directly responsible for its lower Φ_{UC} . Interestingly this observation suggests that while the difference in structure between **1** and **2** has no bearing on TET or FRET, it does impact the cross surface migration and TTA events that are responsible for Φ_{TTA} .

While Φ_{TTA} is larger in **5** than for **2**–**4**, the drastically lower Φ_{FL} and Φ_{out} result in the significantly lower overall emission from the upconverted state of **5**. However, it is worth noting that in an integrated bilayer TTA-UC solar cell, electron injection from the UC state is typically much faster ($\sim 10^{12} \text{ s}^{-1}$)⁴⁶ than the k_r , k_{nr} , or k_{FRET} values reported here ($\sim 10^8 \text{ s}^{-1}$) and may not be affected

by Φ_{FL} and Φ_{out} . As such we anticipate an increased photocurrent from **5** relative to **2**–**4**. Such an observation would emphasize the importance of molecular design in targeting specific applications of TTA-UC. Device measurements for TiO_2 -**A**-Zn-S bilayers containing **1**–**5** are currently underway and will be reported at a later time.

3.4.2 TTA-UC intensity dependence. The emission intensity for ZrO_2 -**A**-Zn-S films with respect to the 532 nm excitation intensity are shown in Fig. 6.^{84,85} All five bilayers exhibited a quadratic (slope = 2) to linear (slope = 1) intensity dependence that is symptomatic of a TTA-UC mechanism.⁸⁵ The quadratic to linear crossover intensities, also known as the I_{th} values,⁸⁴ for ZrO_2 -**A**-Zn-S decrease in the order **3** (880 mW cm^{-2}) $\approx$ **4** (870 mW cm^{-2}) > **2** (790 mW cm^{-2}) > **5** (750 mW cm^{-2}) > **1** (470 mW cm^{-2}).

The I_{th} value is inversely related to several parameters as described in eqn (6):

$$I_{\text{th}} = \frac{1}{\Phi_{\text{TET}} \times \alpha(E) \times (\tau_{\text{A}}^3)^2 \times \gamma_{\text{TTA}}} \quad (6)$$

where τ_{A}^3 is the triplet excited state lifetime of **A**, Φ_{TET} is the TET efficiency, $\alpha(E)$ is the sensitizer absorption cross-section at 532 nm, and γ_{TTA} is the second-order rate constant for TTA.⁴⁶

Following a previously published procedure,⁸⁶ τ_{A}^3 was determined for each **A**, using $\tau_{\text{A}}^3 = 2 \times \tau_{\text{UC}}$, where τ_{UC} is obtained by tail fitting the TTA-UC emission decay at 430 nm for a DMSO solution of **A** and **S** after 532 nm excitation. As can be seen in Table 3, molecules **2**–**4** exhibit similar triplet excited state

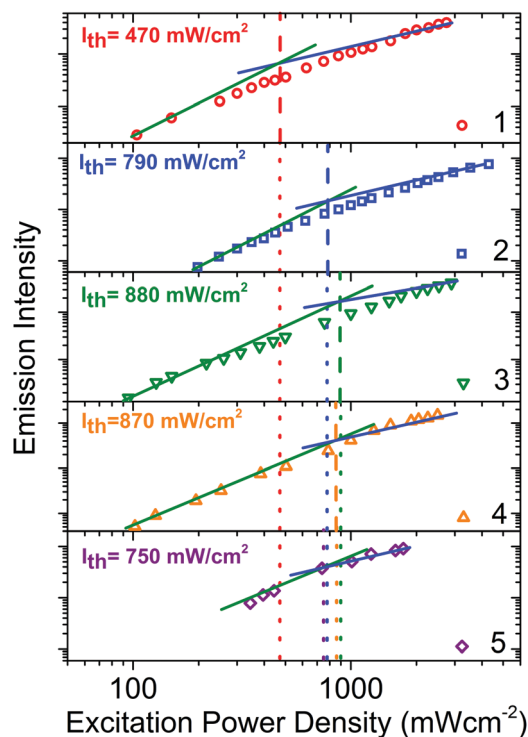


Fig. 6 Emission intensity versus 532 nm excitation intensity for ZrO_2 -**A**-Zn-S in MeCN where **A** = **1**–**5** (slopes of 1 and 2 are denoted by blue and green lines, respectively).

lifetimes on the order of 0.5 ms. In contrast, molecule **5** has the shortest lifetime of 0.07 ms which is in reasonable agreement with its singlet excited state behavior where it has an order of magnitude larger k_{nr} than the other molecules. Similar non-radiative decay channels may be accessible from the triplet state.

Strikingly, **1** has a τ_A^3 that is four times larger than **2–5**. This is particularly remarkable given that **1** and **2** give almost identical singlet excited state energetics and kinetics. It is possible that while the position of the phosphonate group has minimal influence on the singlet manifold, it may perturb the triplet state potential energy surface and lead to subsequent mixing/overlapping between states as previously observed by Gray *et al.*²⁵

Using eqn (6), and the parameters listed in Table 4, γ_{TTA} was calculated for each **A**. γ_{TTA} for ZrO₂-A-Zn-S ranges from $4.4 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ to $1 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$ for **5** and **1**, respectively. Despite **1** having the lowest γ_{TTA} , it has the lowest I_{th} value due to the four-fold larger τ_A^3 , whose exponent of 2 in eqn (6) makes it a more strongly impactful variable in dictating I_{th} than γ_{TTA} . For **5**, the short lifetime is partially offset by the much larger γ_{TTA} , resulting in the second lowest I_{th} value of the series. If one were able to combine the γ_{TTA} of **5** while still retaining the long triplet excited state lifetime of **1**, I_{th} values on the order of the solar flux ($\sim 5 \text{ mW cm}^{-2}$) would be feasible for TTA-UC emission from the bilayer film.

The values for γ_{TTA} in Table 4 are orders of magnitude smaller than for anthracene molecules in solution or crystals.⁴¹ This observation could imply one of two things, either diffusion (*i.e.* the rate of triplet migration across the surface) or the rate of TTA after the triplets have encountered is significantly slower in the bilayer film than in other media. If we assume, as with most other TTA-UC schemes,^{87–89} that the rate limiting process is triplet migration, then the triplet exciton diffusion constant (D) can be calculated using $\gamma_{TTA} = (8\pi D a_0)^{28,84}$ where a_0 is the effective triplet-triplet interaction distance which in this case is assumed to be the intermolecular packing distance on the surface, d_{A-A} . For ZrO₂-A-Zn-S, D increases in the order **5** ($2.0 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) > **4** ($1.4 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$) $\approx$ **3** ($1.7 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$) > **2** ($3.1 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$) > **1** ($4.6 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$) again with **5** and **1** being the upper and lower extremes of this parameter.

The lowest diffusion rate is observed with the diphenyl derivatives **1** and **2**. Presumably the phenyl groups provide some form of hindrance or molecular rigidity that decreases electronic coupling between adjacent molecules. The order of

magnitude difference between **1** and **2** may be a manifestation of how the molecules orient relative to the surface and to adjacent molecules. The origin of the two orders of magnitude higher D for **5** ($2.0 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) is currently unclear to us. One could envision that lower steric hindrance or the forced relative orientation dictated by the methyl groups at the 2,6-position would favour face-to-face stacking of the acceptor molecules. Alternatively, the flexibility afforded by the methyl phosphonate group may allow for additional mobility of the tethered molecule such that it can sample a larger orientation space on the timescales of triplet diffusion. These observations again emphasize the importance of obtaining either experimental or theoretical insights into the molecular structure at the interface. Understanding and then controlling these structural parameters is critical to improving TTA-UC efficiencies in self-assembled systems.

As a somewhat unrelated side note, it was intriguing to us that there is a strong linear correlation ($R\text{-sq} = 0.98$) between the I_{th} values and Φ_{TTA} for this series of molecules (Fig. S7, ESI†). To the best of our knowledge there is no intrinsic or causal reason for this correlation. The values are measured independently and Φ_{TTA} is effectively the y-offset of the intensity dependence graph (*i.e.* the I_{th} curve). We attempted to determine if this was a general trend among TTA-UC systems but unfortunately a majority of the manuscripts that report Φ_{TTA} do not also include the I_{th} values, or *vice versa*, under the same conditions. It is however worth mentioning that if this linear relationship holds true, then increasing Φ_{TTA} to 0.01, for example, would result in an I_{th} value of 5 mW cm^{-2} .

Given its strong impact on both I_{th} and Φ_{UC} , these results indicate that dramatically increasing Φ_{TTA} is a necessary step in increasing the efficiency of TTA-UC in bilayer films. One contribution to Φ_{TTA} is the probability of obtaining a singlet excited state after annihilation of two triplet states, sometimes denoted as f .⁹⁰ Pure spin statistics limit f to only 1/9 ($\Phi_{TTA(\text{max})} = 0.11$).⁹¹ However this fraction can be increased if the quintet state is energetically inaccessible ($\Phi_{TTA} = 0.25$), and even further so if an upconverted triplet state can undergo reverse ISC into the singlet state. Experimental f values as high as 0.66 have been reported.⁹² Presumably, as is well known in singlet fission (SF), or roughly the reverse of TTA, molecular packing could have a profound influence on the rate and thus the efficiency of TTA. However, the role of relative molecular orientation, if any, in dictating f is currently unknown but newly developed

Table 4 I_{th} values, effective triplet-triplet interaction distances (a_0), acceptor triplet lifetimes (τ_A^3), the second-order rate constants for TTA (γ_{TTA}) and triplet diffusion coefficients (D)

	I_{th} (mW cm ⁻²)	$\alpha(E)^a$ (cm ⁻¹)	a_0^b (Å)	τ_A^3 (ms)	γ_{TTA}^d (cm ³ s ⁻¹)	D^e (cm ² s ⁻¹)
1	470	575	8.6	2.02	1.0×10^{-15}	4.6×10^{-10}
2	790	565	9.7	0.55	7.6×10^{-15}	3.1×10^{-9}
3	880	450	16.0	0.48	6.9×10^{-15}	1.7×10^{-9}
4	890	555	11.2	0.62	3.9×10^{-15}	1.4×10^{-9}
5	750	570	8.9	0.07	4.4×10^{-13}	2.0×10^{-7}

^a $\alpha(E) = 5700 \times A_{\text{PtP}(532\text{nm})}$. ^b Estimated as d_{A-A} . ^c $\tau_A^3 = 2 \times \tau_{UC}$ where τ_{UC} is from an exponential tail fit to the upconverted emission decay from **A** (1000 μM) and **S** (0.5 μM) in DMSO ($\lambda_{ex} = 532 \text{ nm}$). ^d $\gamma_{TTA} = 1/[(\Phi_{TET}\alpha(E)\alpha(\tau_A^3)^2 I_{th})]$. ^e $D = \gamma_{TTA}/(8\pi a_0)$.

self-assembled systems may provide a scaffolding to study this relationship.

4. Conclusion

Here we have reported the synthesis and photophysical characterization of phosphonated anthracene derivatives that act as the acceptor molecule in self-assembled bilayers for TTA-UC. The acceptor molecules are composed of an anthracene core functionalized with 9,10- or 2,6-phenyl, methyl, or directly bound phosphonic acid groups for metal ion coordination. In terms of ZrO_2 surface binding, the molecules obey Langmuir isotherm behavior with a maximum surface loading giving a center-to-center packing distance on the order of 10 Å. Binding the molecules to the surface has minimal influence on the photophysical properties of the dyes relative to solution. Increased steric hindrance at the 9,10-positions, as opposed to the 2,6-positions, was found to increase the photostability of the dyes at the interface with the primary decomposition mechanism likely being a reaction with oxygen of the anthracene core.

The acceptor molecules were incorporated into self-assembled bilayer films with zinc as the linking ion and platinum porphyrin as the sensitizer. All five films facilitate green-to-blue photon upconversion with UC efficiencies as high as 0.0023 for **1**. Φ_{TTA} and not Φ_{TET} , Φ_{FL} , or Φ_{out} , was found to be the primary variable limiting the TTA-UC emission efficiency. Films containing compound **1** also exhibited the lowest I_{th} value despite having a lower second-order rate constant for TTA and diffusion constant. Regardless of having similar photophysical properties, variation in the position of the phosphonic acid on diphenylanthracene (**1** versus **2**) resulted in dramatically different Φ_{TTA} , I_{th} values, γ_{TTA} , and D . Molecule **5**, with a methylphosphonic group at the 2,6-position exhibited the highest triplet exciton diffusion rate and γ_{TTA} but they could not compensate for the short triplet lifetime and low fluorescence quantum yield and thus **5** exhibited the least efficient TTA-UC emission. Interestingly, we observed a strong linear correlation between Φ_{TTA} and the I_{th} value but the cause of this relationship, if any, is unclear.

Collectively the results reported here point to three primary conclusions, (1) increasing Φ_{TTA} is the key factor in lowering the I_{th} value and increasing Φ_{UC} in bilayer films, (2) the structure of the molecule, and not simply the energetics, can be, but is not always, a critical factor influencing TTA-UC in the bilayer architecture, and (3) measuring and modelling the structure at these interfaces will be a necessary step in fully explaining and then controlling migration, triplet energy transfer, back energy transfer and ultimately the TTA-UC efficiency in self-assembled bilayer films.

Conflicts of interest

There are no conflicts to declare.

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