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Thermal control of intermolecular interactions and tuning of fluorescent state energies

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Abstract

The prospect to tune the energy of emitting states through external stimuli opens the possibility to shift the energy of emitting units on demand and control the bimolecular processes they are involved in. To prove this concept, the fluorescence properties of three differently 9,10-substituted anthracene derivatives are investigated in a phase change material (eicosane). The liquid-to-solid transition of the medium leads to an increase of the local dye concentration, a shortening of the intermolecular distances and the establishment of excited and ground-state interactions. As a result, a new contribution to the overall luminescence derives from the downshifted emission (up to 0.7 eV) from excimer-like species is observed. The addition of a second dye (a Pt-porphyrin) reduces the efficiency of excited and ground-state complexes between fluorophore units, although does not prevent the formation of multichromophoric aggregates where interactions between Pt-porphyrin and the emissive state of anthracene derivatives are observed.

KEYWORDS. Phase change materials, fluorescence, aggregation, excimer, excited states energy modulation

Introduction

In properly designed systems, the control of homochromophoric intermolecular distances or interactions can modify the nature of the lowest excited states, which affects the efficiency, and interestingly, the energy of emitted radiation.^{1,2} On the other hand, by controlling the energy of the luminescent state, the management of the rate and the efficiency of heterochromophoric bimolecular processes involving the excited states can be achieved. For instance, the luminescence originating from non-linear processes, such as the anti-Stokes emission of upconverting molecular materials, can be modulated in this way. In particular, triplet-triplet annihilation based upconversion (TTA-UC) requires intermolecular energy transfer among the excited states of donors and acceptors and these interactions can be manipulated by tuning the energy of their emitting states. This is valid not only for liquid solutions but also for solid materials, where the energy migration through molecular aggregates^{3,4} emerged as an alternative strategy to overcome the lack of molecular diffusion^{5,6} and allow TTA-UC in the solid phase.

We have previously exploited the aggregation phenomenon of the donor units in aliphatic phase change materials (PCMs) to achieve thermally switchable TTA-UC.⁷ While negligible energy transfer processes and, as such, red phosphorescence from the donors were observed in the liquid state of the system at relatively low dye concentrations, blue upconverted emission was registered upon solidification of the medium. This was due to chromophore aggregation in the solid PCM, which facilitated the energy transfer processes that underlie TTA-UC. Though we demonstrated the very efficient triplet-triplet energy transfer process between sensitizers and emitters ($\Phi_{ET} > 95\%$) in the solid PCM and the role of sensitizer aggregates, we did not explore the occurrence of interactions among the emitter units and their impact on the energy of their emitting state.

Notably, the fluorescence of the emitters is able to report on intermolecular interactions occurring on the singlet state but also on the triplet manifold. For instance, bimolecular interactions or extended aggregation can stabilize singlet and triplet states thus fastening energy transfer or energy migration. These interactions can enhance the efficiency of triplet energy transfer (up to $\Phi_{TRET} \sim 0.9$) involved in TTA-UC and explain the high UC quantum yield ($\Phi_{UC} \sim 0.06$)⁷ observed below the PCM melting point (T_m). Furthermore, the outcome of careful analysis of the fluorescence data could be easily extended to many fundamental processes.

In view of this, we investigate herein the fluorescence properties of anthracene dyes (frequently used as emitters in TTA-UC) as a function of the PCM phase and we further extend these studies in the presence of 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine platinum(II) (PtOEP), usually employed as an antenna to sensitize TTA-UC. The modifications of the fluorescence spectra and decay times should provide information on the ground and/or excited state intermolecular interactions and document changes of their singlet state energies, which have the same behaviour as the corresponding triplet states, according to literature data.⁸⁻¹¹ To this aim, we select three anthracene derivatives with different 9,10-substituents (Scheme S1); the 9,10-substitutions can significantly alter the π - π intermolecular interactions occurring in the ground and/or excited state but, according to experimental data and DFT calculations, only induce minimal changes of the energies either in the singlet and triplet manifold. Eicosane (EC), an aliphatic paraffin already used in our previous work, is chosen as a PCM ($T_m=37$ °C).¹²

Experimental section

Materials. 9,10-diphenylanthracene (**DPA**), 9,10-dimethylantracene (**DMA**, 99%, EGA Chemie), anthracene (**ANT**, 99%, J. T. Baker), 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphine platinum(II) (**PtOEP**, 98%, Sigma Aldrich) were used without further purification. Dichloromethane (DCM, $\geq 99.5\%$) has been provided by Alfa Aesar. Eicosane (EC, 98%, melting temperature, $T_m = 37\text{ }^\circ\text{C}$) was purchased from Merck and used as received.

Solutions preparation. Stock solutions of DPA ($[\text{DPA}]_0 = 1.35\text{ mM}$), DMA ($[\text{DMA}]_0 = 3.5\text{ mM}$), ANT ($[\text{ANT}]_0 = 0.53\text{ mM}$) and PtOEP ($[\text{PtOEP}]_0 = 0.12\text{ mM}$) were prepared in dichloromethane and stored in the dark to prevent any photodegradation. The proper amount of the stock solution was added to the weighted quantity of EC ($\rho_{\text{EC}}^{20^\circ\text{C}} = 0.7886\text{ mg/mL}^{13}$) to obtain the desired concentration of the dyes in EC. After the addition of DCM to EC, the mixture was stirred and warmed above the melting temperature of the PCM, thus allowing the homogenization of the system. The complete removal of volatile DCM was thus achieved. The samples were transferred into cuvettes to perform the photophysical analysis. In the sample containing both DPA (or, alternatively, DMA or ANT) and PtOEP, the molar ratio between the two dyes was set at 30:1.

Photophysical characterization. The fluorescence emission and excitation spectra have been recorded on a Fluorolog-Spex F112AI spectrofluorometer equipped with a Xenon lamp as an excitation source and a temperature-controlled sample holder. The spectra have been acquired in front face configuration (with a 23° angle between the excitation light and the detector) and have been corrected for the instrumental response. The emission spectra have been corrected for the self-absorption effect, as reported in ref. 14. Fluorescence decay times were measured by the single photon counting method using an Edinburgh Instrument 199S setup. A 370 nm nanoLED with a 0.2 ns pulse duration was used as an excitation source and the signal was acquired by a

Hamamatsu R7400U-03 detector. The decays have been collected using a 45° configuration between the excitation light and the detector.

Results and Discussion

Anthracene (**ANT**) in liquid EC presents well-structured emission and excitation spectra (Figure 1) in agreement with the literature data.¹⁵ The liquid-to-solid transition of the medium results in dramatic spectral changes. The emission spectrum of **ANT** in solid EC preserves its vibronic structure, though the relative intensities of the bands are strongly altered and a new broad band centered at 510 nm appears (Figure 1b). The excitation spectrum loses its characteristic vibronic structure and becomes broadened (Figure 1a). The comparison with literature data supports the assignment of the 510 nm band to the **ANT** excimer,¹⁶ whose formation is also confirmed by the overlap of the excitation spectra recorded at 443 and 510 nm (Figure S2). The phase change of the medium also affects the fluorescence decay of **ANT** (Figure S1 and Table S1). The mono-exponential behavior observed in liquid EC ($\tau = 5.1$ ns) is attributable to the monomeric species, while in the solid sample the decay has a bi-exponential behavior with decay times that vary with the emission wavelength. The shorter decay time for the monomeric emission (0.8 and 2.2 ns at 418 nm), was ascribed to the quenching of the excited state due to the formation of excimer species, to which corresponds longer decay times at 510 nm (1.4 and 5.2 ns). Thus, upon EC solidification, the emission spectrum documents that excited state intermolecular interactions are established, although ground state aggregation cannot be excluded to account for the changes in the excitation spectra. Considering the emission maximum of the monomer in liquid eicosane (3.1 eV) and the maximum of the excimer emission

(2.4 eV), obtained in the solid medium, we conclude that a new emitting state, 0.7 eV downshifted compared to the monomer, raises upon PCM solidification.

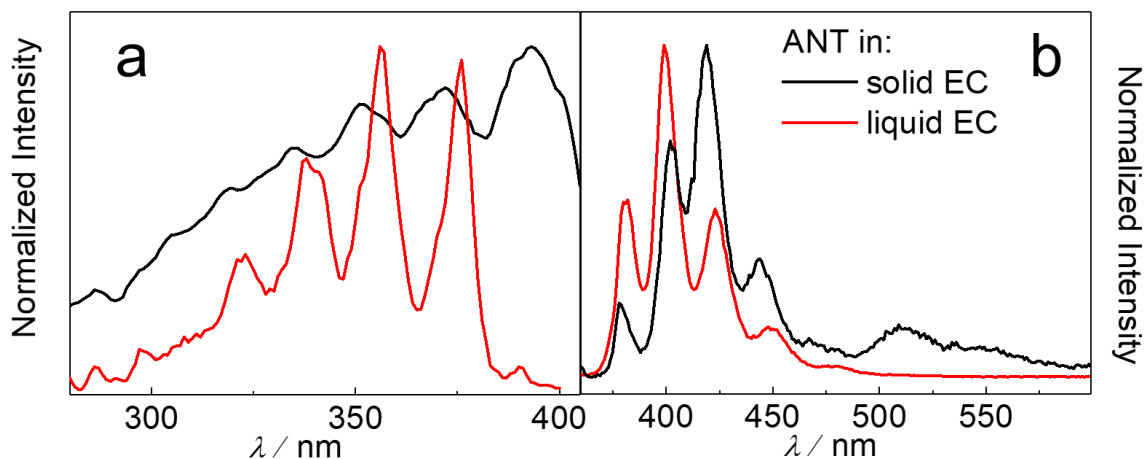


Figure 1. (a) Normalized excitation ($\lambda_{\text{em}} = 418$ nm) and (b) emission spectra ($\lambda_{\text{exc}} = 326$ nm) of ANT ($[\text{ANT}] = 0.11$ mM) in liquid and solid EC.

When the emitter has bulky substituents tethered to the anthracene core, as in the case of 9,10-diphenylanthracene (**DPA**), the liquid to solid transition of EC produces notable but dissimilar changes of the fluorescence behaviour. Once EC solidifies, the excitation spectrum (Figure S3a) broadens and loses the vibronic structure characteristic of monomeric **DPA**,¹⁷ while the emission spectrum (Figure S3b) is essentially unaltered. In contrast to ANT, this suggests that, although ground-state interactions do take place between DPA molecules in solid EC,¹⁸ neither excimer-like species formation nor emission energy variation occur. We ascribe these results to the steric hindrance imparted by the large phenyl substituents, which impede achieving sufficiently short interchromophoric distances as to enable for excited state interactions. Actually, the ground state

aggregation of **DPA**-analogues has been already observed,¹⁸ but at fluorophore concentrations at least one order of magnitude higher.

When 9,10-dimethylantracene (**DMA**) is used as an emitting unit, both ground-state aggregates and excimers are formed in solid EC. In liquid EC, the structured monomeric emission is observed (Figure 2a) and it has a monoexponential decay whose decay time (10.3 ns) well matches the value reported for **DMA** in homogeneous solutions.¹⁹ After cooling the PCM below the T_m , in addition to the structured emission spectrum (390 - 520 nm), the appearance of a broader band centered at 550 nm is observed (Figure 2a). The latter is due to excimer-like species,²⁰ as indicated by the good overlap of the excitation spectra collected at 427 and 540 nm (Figure 2b). Furthermore, the concomitant broadening of the excitation spectra stands for the presence of ground-state aggregates in the solid medium. In the case of **DMA**, the energy of the lowest fluorescence state shifts from 2.9 eV to 2.2 eV going from liquid to solid EC.

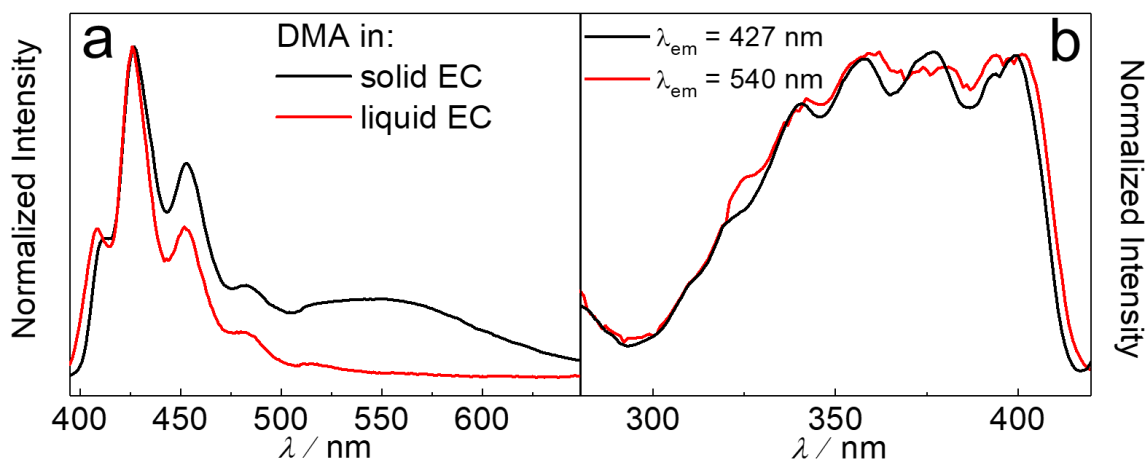


Figure 2. (a) Normalized emission spectra ($\lambda_{exc} = 372$ nm) of **DMA** in solid and liquid EC. (b) Normalized excitation spectra recorded at the monomer ($\lambda_{em} = 427$ nm) and excimer ($\lambda_{em} = 540$ nm) emission maxima in solid EC ($[\mathbf{DMA}] = 1.50$ mM).

Time-resolved measurements confirmed that DMA excimer-like species are formed when EC solidifies. Below T_m the monomer average lifetime decreases significantly ($\tau_{\text{mean}} = 5.5$ ns) and its decay curve could be reproduced by a bi-exponential function (Figure 3, Table S2), confirming the interaction of the excited state, similarly to what observed for **ANT**. On the other hand, a non-exponential emission decay with much longer average lifetime (53.2 ns) was collected in the excimer region ($\lambda_{\text{em}} = 560$ nm), in agreement with the literature data.²¹

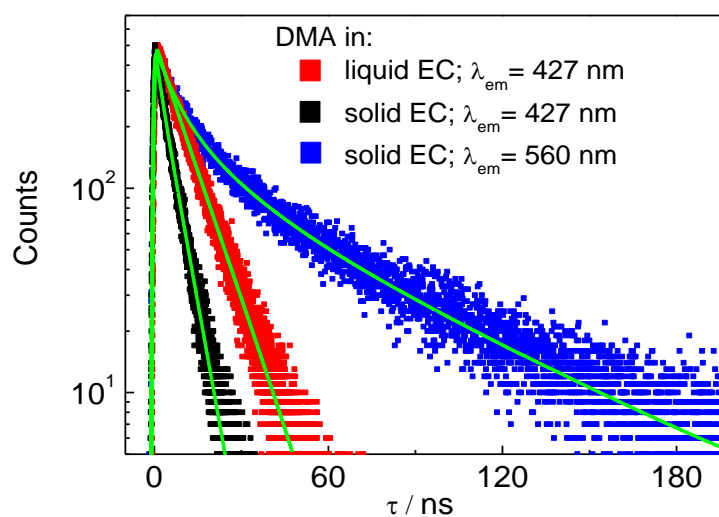


Figure 3. Emission decay curves of **DMA** in liquid and solid EC. The green lines represent the fitting curves of the experimental points ($[\text{DMA}] = 1.50$ mM; $\lambda_{\text{exc}} = 370$ nm).

The spectral and decay times modification observed for **ANT**, **DMA** and, in a lesser extent, **DPA** when passing from liquid to solid EC can be attributed to the shortening of the intermolecular distances and to the increase of local fluorophore concentration enabling the occurrence of ground and/or excited state interactions, as already reported for aromatic

molecules in aliphatic media.²² In fact, the PCM liquid-to-solid transition brings spectral modifications analogous to those obtained when increasing the dye concentration (Figure S4-S7).

The presence of other types of chromophores can interfere with the arrangement of the emitting units in the aggregates formed in solid phase EC, thus altering the resulting intermolecular interactions and, as a result, impacting on the energy and kinetic properties of the fluorophore excited states. To verify this hypothesis, we decided to introduce PtOEP (a typical sensitizer for TTA-UC) as an additional chromophore to the anthracene derivatives/EC solutions, choosing a PtOEP/emitter molar concentration ratio (1/30) normally used in TTA-UC systems.²³

In the presence of PtOEP, the emission spectrum of **ANT** in solid EC lacks the 510 nm band (Figure 4a-b), indicating that the formation of excimer-like species is inhibited by addition of the porphyrin molecules. At these conditions, however, the establishment of interactions between PtOEP and the excited state of **ANT** is confirmed by the shortening of the fluorescence lifetime (quenching) (Figure S8 and Table S3), which reveals that chromophore aggregation does still take place.

The partial structuration of the **DPA** excitation spectrum and the minor modification of the **DPA** emission spectrum observed in the presence of PtOEP indicate that porphyrin addition also reduces the **DPA** ground-state interactions resulting from aggregation (Figure 4c-d). On the other hand, porphyrin effect on the **DPA** excited singlet manifold is negligible, since the emission spectrum is not modified by the presence of PtOEP. The present data indicate that the efficient UC-emission observed in solid PCM for PtOEP-DPA mixtures⁷ is mainly due to the presence of ground-state heterocomplexes which can facilitate energy transfer processes (e.g. *via* triplet

migration).^{3,4} The nature of these complexes and the interaction mechanism deserve deeper investigations.

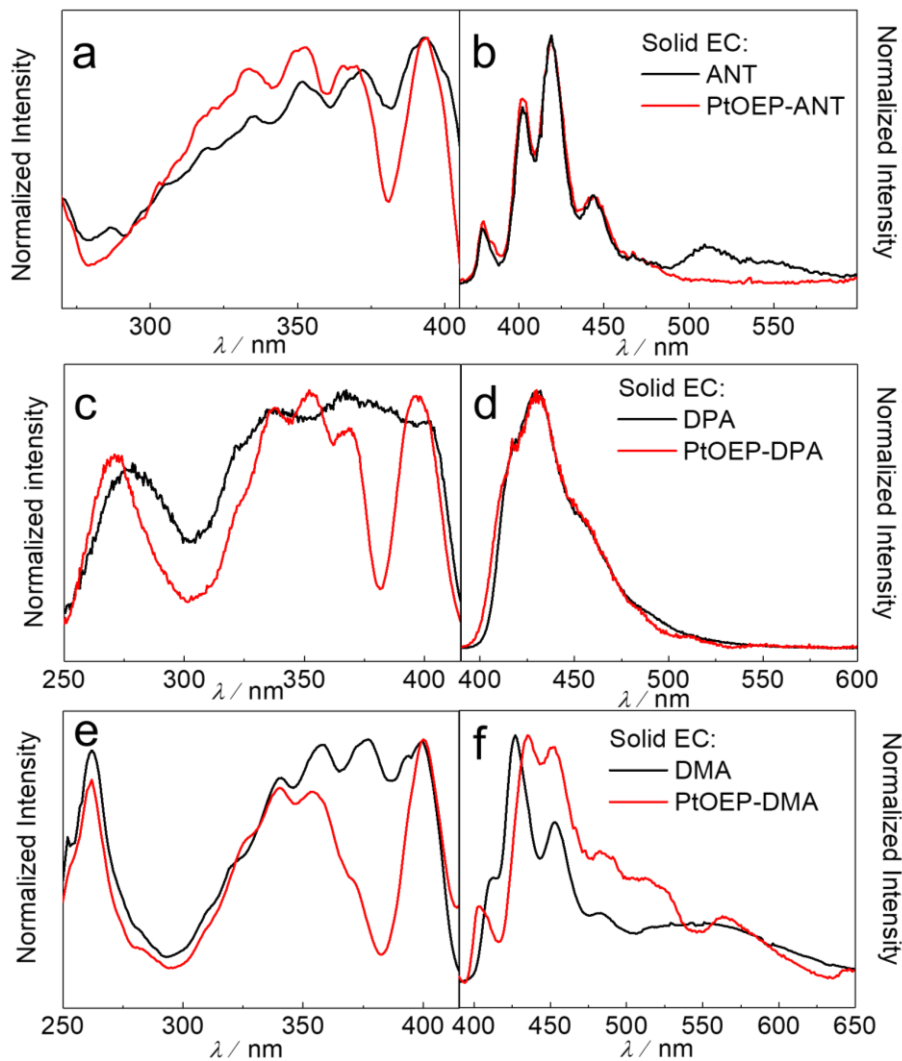


Figure 4. (a) Normalized excitation ($\lambda_{em} = 443$ nm) and (b) emission ($\lambda_{exc} = 326$ nm) spectra of **ANT** and **PtOEP-ANT** ($[ANT] = 0.11$ mM; $[PtOEP] = 3.7$ μ M). (c) Normalized excitation ($\lambda_{em} = 430$ nm) and (d) emission spectra ($\lambda_{exc} = 372$ nm) of **DPA** and **PtOEP-DPA** in solid EC ($[DPA] = 1.35$ mM; $[PtOEP] = 45$ μ M). (e) Normalized excitation ($\lambda_{exc} = 430$ nm) and (f) emission ($\lambda_{exc} = 372$ nm) spectra of **DMA** in solid EC in the absence and presence of **PtOEP**

([DMA] = 1.5 mM; [PtOEP] = 45 μ M). (The valley at 380 nm is due to the re-absorption of PtOEP).

The data collected on the **PtOEP-DMA** system (Figure 4e-f) demonstrate that, in the presence of the porphyrin, both the excimer and the monomer emission bands are preserved, though they appear modified. The presence of PtOEP mainly affects the excited states of the emitter. Decay time measurements (Figure S9, Table S2) performed in the presence of **PtOEP** reveal that whereas in liquid EC the **DMA** decay is not affected by the porphyrin, a clear shortening of excimer emission (up to 4 times) in solid EC is observed. This behaviour documents the interactions between the excited **DMA** (monomer and excimer) and PtOEP, when the dyes are at short distance.

Conclusions

In summary, we have investigated the fluorescence behaviour of three anthracene derivatives to rationalize the impact of medium phase change on the interchromophoric ground and excited state electronic interactions. While in the liquid state the dyes all show the monomeric fluorescence features, indicating lack of intermolecular interactions, in the solid state, these interactions are established at low dye concentrations (\leq mM). The electronic state involved depends on the substituents: ground-state aggregates are observed for **DPA** while both ground-state aggregates and excimers are detected for **ANT** and **DMA**, with the latter forming excimers predominantly. In the latter case, the formation of excimer-like species results in changes in the energy of the emitting state of about 0.7 eV and this shift is preserved even in the presence of an interfering dye. We demonstrate that by simply changing the temperature from above to below

the melting point of PCM the tuning between monomer to excimer (and/or aggregate) emission can be produced.

Supporting Information. The Supporting Information, containing supplementary figures, is available free of charge on <http://pubs.acs.org>

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Notes

The authors declare no competing financial interests.

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TOC GRAPHICS

