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COMMUNICATION

Chain confinement promotes β -phase formation in polyfluorene-based photoluminescent ionogels†Rachel C. Evans^{*a} and Patricia C. Marr^{*b}

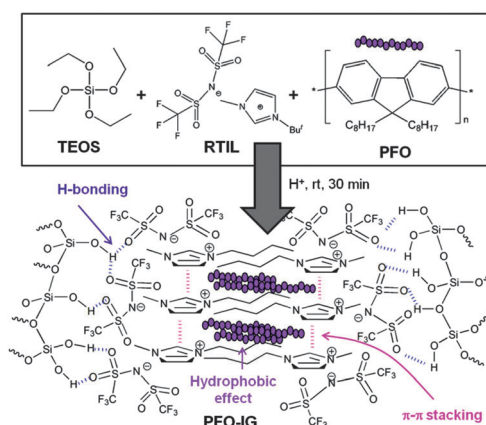
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The synthesis of photoluminescent conjugated polymer silica ionogels using sol-gel chemistry is described. Cooperative self-assembly of an ionic liquid, the silica precursor and poly(9,9-dioctylfluorene) (PFO) via hydrogen bonding and π -stacking interactions drives formation of the PFO β -phase.

Simultaneous control of both the morphology and electronic properties of conjugated polymers (CPs) is an important goal for their application in optoelectronic devices. CP organic-inorganic hybrids represent an elegant approach to indirect manipulation of the polymer conformation and orientation.^{1,2} Multiple physical interactions (*e.g.* hydrogen bonding, ionic, π - π stacking) at the organic-inorganic interface can be harnessed to ensure homogenous mixing of the two components on the macroscale, whilst simultaneously promoting nanoscale phase separation at the active interface.³ The optical and charge transport properties of CPs are critically dependent on their conformation. Controlled interfacial engineering may therefore provide a route to improved device efficiency.

It has previously been shown that room temperature ionic liquids (RTILs) can be used as templates upon which mesoporous silica can be constructed.⁴ Antonietti and co-workers proposed that a hydrogen bond *co*- π - π stack mechanism at the RTIL-silica interface resulted in the formation of wormlike mesopores after template removal.^{4c} We postulated that this phenomenon could be exploited (for the first time) in the rational, selective engineering of a CP-RTIL-inorganic hybrid, in which cooperative interactions at the phase interface promote localisation of the three components (*i.e.* silica, RTIL and CP) within either hydrophilic or hydrophobic domains. We reasoned, that on addition of a CP to this system, the CP should preferentially occupy the hydrophobic environment created by π - π stacking interactions between [Bmim]⁺ cations (Scheme 1), which would drive polymer aggregation in an ordered fashion. Thus, specific interactions between the RTIL and the CP could be



Scheme 1 Representation of the proposed stacking mechanism that promotes β -phase formation in PFO-IG.

used to carefully manipulate the polymer conformation. If, after synthesis, the RTIL would be incorporated as a functional component of the hybrid, the resulting material would be classified as an *ionogel* (IG).^{5a} Ionogels have been demonstrated as attractive host materials for photo-, electro-active and catalytic species.^{5,6} To test this hypothesis, we began by attempting to devise a facile synthetic route to CP-ionogels from the sol-gel reaction of the silica precursor tetraethyl orthosilicate (TEOS) in the presence of the RTIL 1-butyl-3-methyl-imidazolium bis(trifluoromethanesulfonyl)imide [Bmim]⁺[Tf₂N][−] and a CP (Scheme 1). We chose to focus on the CP-ionogel prepared from poly(9,9-dioctylfluorene) (PFO-IG), since the optical properties of PFO are known to be highly dependent on morphology and, as such, can be used as a diagnostic probe of polymer conformation.⁷ Gratifyingly, upon synthesis of the material, subsequent photophysical characterisation of PFO-IG provided evidence for formation of the PFO β -phase, in which individual PFO chains adopt a planar, stacked conformation.^{7–10} To the best of our knowledge this is the first observation of PFO β -phase formation in a hybrid material.

In a typical synthesis, a volume of PFO stock solution ($M_n \sim 15\,000$ g mol^{−1}; 1 mg mL^{−1} in CHCl₃) was added to a mixture of TEOS (1.0 mL, 4.41×10^{-3} mol) and [Bmim]⁺[Tf₂N][−] (1 mL, 3.43×10^{-3} mol) and stirred for 30 min. Formic acid (2 mL, 5.3×10^{-2} mol) was then added, whilst stirring (TEOS: formic acid: IL mole ratios 1 : 1 : 2). The gelation time was less than 40 min. The gel was covered and

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† Electronic Supplementary Information (ESI) available: PL spectrum of BL-IG, FTIR spectra of RTIL and BL-IG, powder XRD patterns, ¹³C and ²⁹Si MAS-NMR spectra, PL spectra of CP-IG's, assignment of FTIR data. See DOI: 10.1039/c2cc18022g

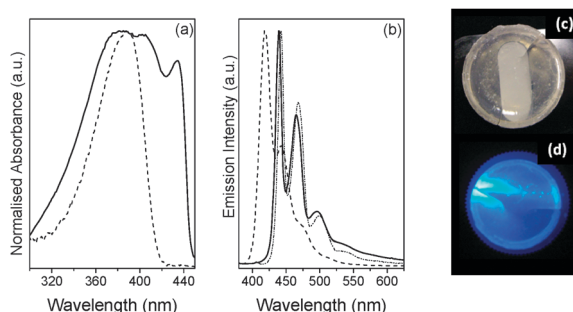


Fig. 1 (a) Absorption/excitation and (b) photoluminescence (PL) spectra for PFO in CHCl_3 (dashed line) and **PFO-IG** (solid line). The PL spectrum for **PFO-IG** following mechanical compression is also shown (dotted line) ($\lambda_{\text{ex}} = 370$ nm). (c) and (d) show **PFO-IG** in natural light and under $\lambda_{\text{ex}} = 370$ nm, respectively.

aged for 28 days. The resulting ionogel **PFO-IG** was obtained as an optically transparent monolith (Fig. 1). A blank ionogel sample (**BL-IG**) (containing no PFO) was also prepared.

Fig. 1 shows the UV/vis absorption, photoluminescence (PL) and excitation spectra for the precursor PFO solution and **PFO-IG**. In chloroform, PFO adopts a rigid rod-like conformation, comprised of individually-dissolved chains.⁹ The absorption spectrum exhibits a broad, unstructured band ($\lambda_{\text{max}} = 388$ nm), attributed to the disordered α -phase. The corresponding PL spectrum displays the characteristic polyfluorene emission profile, featuring a well-structured peak between 400–500 nm. In contrast, the new material **PFO-IG** possesses remarkably distinct properties relative to its precursor, which are optically characteristic of the PFO β -phase. The excitation spectrum exhibits an additional, red-shifted peak at 435 nm. Moreover, the PL spectrum is significantly red-shifted, with improved resolution of the vibronic structure. Red-shifted absorption and emission are characteristic of the β -phase, due to extended π -conjugation and increased rigidity in the more planar morphology.^{7,8} The absence of emission associated with an α -phase conformation, combined with the continued presence of the broad absorption band, suggests that efficient Förster energy transfer occurs from α -phase domains to lower energy β -phase aggregates within **PFO-IG**. It is noteworthy, that once formed, the β -phase remains stable within the ionogel; mechanical compression (~ 10 megagrams) has a negligible effect on the PL spectrum (Fig. 1b).

The PFO β -phase is most commonly observed in polymer thin films that have been subjected to specific thermal or vapour treatment, or have been cast from a poor solvent.⁸ β -phase formation has also been observed in PFO supramolecular gels in apolar organic solvents.¹⁰ A third γ -phase, attributed to a physically cross-linked 3D network, was also observed in these gels;¹⁰ however we find no evidence for its formation in **PFO-IG**. Ionogels and other silica-derived composites containing the RTIL $[\text{Bmim}]^+[\text{Tf}_2\text{N}]^-$ have been reported to exhibit intrinsic broad band photoluminescence in the spectral region 360–500 nm.¹² We also observe weak PL in this region for **BL-IG** (Fig. S1, ESI†). The PL quantum yields (PLQY) for **PFO-IG** and **BL-IG** differ significantly (16% and 2.5% ($\pm 10\%$), respectively), however, which when considered in conjunction with the diagnostic optical characteristics of the PFO β -phase, enables us to eliminate this intrinsic PL as

the origin of the observed spectral shifts for **PFO-IG**. We note that the PLQY for **PFO-IG** is considerably lower than both the literature values for PFO in CHCl_3 (81%)¹¹ and for the β -phase in spin-cast films (55%).^{8a} We would suggest that this strongly indicates that non-radiative decay pathways dominate relaxation of the excited state for **PFO-IG**, potentially due to the presence of structural defects associated with the silica network that behave as energy sinks.

Fig. 2 shows the FTIR spectra of the neat RTIL, **BL-IG** and **PFO-IG**. Detailed peak assignments can be found in Table S1 (ESI†).¹³ While the FTIR spectra of **PFO-IG** and **BL-IG** are similar, four distinct spectral changes are identified when the neat RTIL and **BL-IG** are compared: (I) The $\nu_{\text{C-H}}$ stretching modes ($2850\text{--}3200\text{ cm}^{-1}$) are broadened and shifted to lower wavenumbers on confinement of the RTIL within **BL-IG** (Fig. S2, ESI†). This has been attributed to π - π stacking of the imidazolium ring, which decreases the electronic density of the C-H bond.^{4c} (II) The $1500\text{--}1650\text{ cm}^{-1}$ region is assigned to in-plane symmetric and asymmetric stretching modes ($\nu_{\text{C-N}}$) (imidazolium ring).¹³ In **BL-IG** the broad band at 1570 cm^{-1} is resolved into two distinct peaks (Fig. S3, ESI†). (III) The $\nu_{\text{C-N}}$ ring in-plane stretch (1171 cm^{-1}) is blue-shifted in **BL-IG**. (IV) The $\nu_{\text{C-N}}$ ring bending mode (856 cm^{-1}) is absent in **BL-IG**. When considered together, the observed spectral variations are indicative of the RTIL adopting a more rigid, planar conformation when confined within **BL-IG**, which is consistent with π - π stacking of the imidazolium ring. However, conclusive structural characterisation of **PFO-IG**, and in particular, resolving individual contributions from each component, is challenging. Powder XRD reveals an amorphous silica network is present (Fig. S4, ESI†). ²⁹Si MAS NMR indicates the presence of predominantly Q^3 ($\equiv\text{SiO})_3\text{SiOH}$, -102 ppm) and Q^4 ($\equiv\text{SiO})_4\text{Si}$, -111 ppm) silicon species (Fig S5, ESI†). The degree of condensation, C , (estimated from $C(\%) = 1/4(\%Q^1 + 2\%Q^2 + 3\%Q^3 + 4\%Q^4)$) was determined to be $\sim 85\%$ for both **PFO-IG** and **BL-IG**, which is reduced in comparison to the typical 100 mol% silica glass ($C > 90\%$).¹⁴ This suggests that complete condensation of silica network is restricted by the presence of the RTIL and PFO. ¹³C MAS NMR could only be obtained under direct excitation, indicating that the RTIL essentially behaves as a liquid in the IG (Fig. S5, ESI†).

The driving force for β -phase formation may arise from a number of contributions. Physical confinement will be important: condensation of the silica sol and solvent evaporation will both reduce the mean free volume and generate solubility fluctuations, driving PFO aggregation. However, physical interactions between the RTIL, silica and PFO are likely to

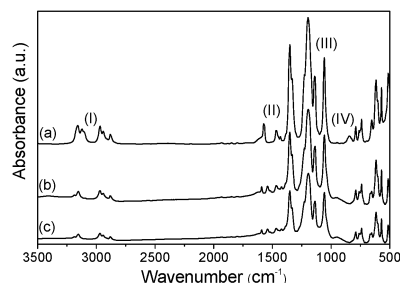


Fig. 2 FTIR spectra of (a) neat RTIL, (b) **BL-IG** and (c) **PFO-IG**.

be the dominant factor in determining the co-organisation of the three components within the final material. Based on the spectral data, we propose that β -phase formation in **PFO-IG** is driven by a similar mechanism of cooperative π - π -stacking, hydrogen bonding and hydrophobic interactions (Scheme 1) as that reported previously for the templated synthesis of mesoporous silica with the related RTIL $[\text{C}_4\text{Mim}]^+[\text{BF}_4]^-$.^{4c} Dissolved water molecules are known to interact directly with the anions of RTILs, forming linear hydrogen bonds.¹⁵ Zhou *et al.* proposed that free silanol groups function as *pseudo*-water molecules, such that hydrogen bonding results in directed orientation of the anion along the pore wall.^{4c} Given that the hydrogen bonding strengths of $[\text{BF}_4]^-$ and $[\text{Tf}_2\text{N}]^-$ are of a similar order of magnitude¹⁵ and that ²⁹Si MAS NMR confirms the presence of Si-OH groups, it seems plausible that a similar interaction operates in **PFO-IG**. The cation $[\text{Bmim}]^+$ is cooperatively aligned along the silica phase, driven by coulombic interactions between the oppositely charged ions and π - π stacking interactions between the imidazolium rings. We propose that aggregating PFO co-assembles with $[\text{Bmim}]^+$, slotting into vacant gaps in the $[\text{Bmim}]^+$ 'ladder'. Polymer chain confinement within the $[\text{Bmim}]^+$ hierarchy thus promotes β -phase formation. A heterogeneous distribution of sites is anticipated, such that α -phase domains may also be present.

In summary, we have reported the targeted formation of the PFO β -phase in **PFO-IG** via selective interfacial engineering. It is noteworthy that our synthetic route is not restricted to **PFO-IG**. We have also prepared iongels incorporating CPs of different molecular weights and structural motifs (Fig. S6–8, ESI). The PL properties of the parent CP were retained in all instances, with no indication of macroscopic phase separation. Binary stable systems of RTILs and CPs have already been shown to meet the photo- and electrochemical requirements of light-emitting electrochemical cells¹⁶ and quasi-solid dye sensitised solar cells.¹⁷ Efficient charge injection and transport is facilitated by homogenous mixing of the two components on the macroscale, co-existing with a nanostructured interpenetrating network at the active interface. The co-operative self-assembly mechanism proposed here for **PFO-IG** may provide a route to interfacial engineering in such systems, leading to the design of more efficient light-emitting and light-harvesting scaffolds.

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