

Suppression of Green Emission in a New Class of Blue-Emitting Polyfluorene Copolymers with Twisted Biphenyl Moieties**

By Shuang-Fang Lim, Richard H. Friend, Ian D. Rees, Jian Li, Yuguang Ma, Kay Robinson, Andrew B. Holmes, Emmanuelle Hennebicq, David Beljonne, and Franco Cacialli*

The color purity of polyfluorene-based blue-emitting polymers is often compromised by “long-wavelength” green emission bands, attributed to polymer interchain species first and more recently to formation of emissive fluorenone defects. Here, we study the nature and the suppression of such bands via characterization of a new class of polyfluorene derivatives modified by insertion of functional groups at the bridging points (position C9), so as to increase inter-ring torsion angles. We find that the solid-state photoluminescence spectra of random copolymers of the modified polyfluorenes and the homopolymer display a progressive decrease of the long-wavelength emission. Electroluminescence spectra also show efficient suppression of such bands in the copolymers with a concentration of ‘twisted’ comonomer units of 40 % or greater. Quantum-chemical calculations on model oligomers address the influence of the bridging unit on the torsion angles, and the resulting excited-state properties; the impact on molecular packing is also explored with force-field calculations. We conclude that increase of intra-biphenyl torsion angles is a viable strategy for suppression of long-wavelength emission bands in polyfluorenes.

1. Introduction

Since the discovery of electroluminescence (EL) in conjugated polymers,^[1] much research has concentrated on achieving high-performance blue emitters to allow fabrication of full-color displays, required for a variety of applications. Although blue-emitting derivatives of poly(*p*-phenylene vinylene), PPV, can be obtained by limitation of the conjugation,^[2] these have not been the materials of choice, because of a number of down-

sides, including the well-known vulnerability of PPVs to rapid oxidative degradation.^[3] Poly(*p*-phenylene), PPP, is also suitable for blue emission,^[4] but addition of solubilizing alkyl substituents introduces steric strain and further twists the phenyl groups out of conjugation, thus yielding violet-blue emitters.^[5] The conjugation length is more extended in ‘ladder-PPPs’ (LPPPs), where neighboring phenyl rings are connected through bridging bonds.^[6] These force a flat π -system, and result in emission not sufficiently blue for applications.^[7] Furthermore, the planarization increases the polymer tendency to aggregate, leading, in some cases, to yellow emission.^[8]

Polyfluorenes have recently emerged as the most attractive blue-emitting polymers due to high efficiency and thermal stability.^[9] Polyfluorenes, like LPPPs, are ‘stepladder’ polymers, in which bridging of neighboring phenylene groups induces planarization of the π -electron system. However, unlike LPPP, poly(fluorene-2,7-diyl) consists only of *pairs* of phenylene rings locked into a coplanar arrangement, and blue emission is preserved more efficiently. Furthermore, functionalization at the C9 atom, such as substitution of solubilizing alkyl groups, can be conveniently placed without introducing excessive torsional strain. Whereas initial synthesis used oxidative routes,^[10,11] researchers at Dow Chemical have recently optimized a modified Suzuki coupling which allows preparation of high-quality polymers and of perfectly alternating copolymers. By providing stable copolymers emitting across the visible range with high efficiency, Dow’s process has propelled polyfluorenes to the forefront of industrial interest.^[9]

Nevertheless, the potential of such materials for application in the blue spectral region is still limited by the appearance of red-shifted luminescence bands.^[12] These have been attributed first to emission from interchain states, possibly induced by thermal annealing or current flow,^[13–16] and facilitated by the planar configuration of the fluorene dyads, still allowing close proximity of the polymer chains. In this scenario, the formation

[*] Dr. F. Cacialli
Department of Physics and Astronomy, University College London
and London Centre for Nanotechnology
Gower Street, London WC1E 6BT (UK)
E-mail: f.cacialli@ucl.ac.uk

Dr. S.-F. Lim, Prof. R. H. Friend
Department of Physics, Cavendish Laboratory, University of Cambridge
Madingley Road, Cambridge CB3 0HE (UK)

Dr. I. D. Rees, Dr. J. Li, Dr. Y. Ma, Dr. K. Robinson,
Prof. A. B. Holmes^[†]

University Chemical Laboratory, University of Cambridge
Lensfield Road, Cambridge CB2 1EW (UK)

Dr. E. Hennebicq, Dr. D. Beljonne
Laboratory for Chemistry of Novel Materials
University of Mons-Hainaut
Place du Parc 20, B-7000 Mons (Belgium)

[†] Current address: Bio21 Institute/CSIRO, University of Melbourne,
Parkville Vic 3010, Australia.

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of 'interchain excited species' is connected with a greater energy delocalization than otherwise possible, thus resulting in a red-shifted and reduced-efficiency emission.^[11–13,15,17] Alternatively, a potential contribution of fluorenone defects to green emission bands in polyfluorenes had been identified since 1998.^[16] Recently, clear new evidence has also been reported proving that fluorenone defects can produce low-energy peaks such as the ones observed in the luminescence spectra of different types of polyfluorenes,^[18] thus calling into question the 'excimer assignment'. As originally pointed out by the IBM researchers,^[16] we also note that the presence of fluorenone defects and of interchain states are not mutually exclusive, but that both may contribute to the observed effects, especially considering the difficulties in uniquely assigning the emission peaks, owing to the fact that excimer and fluorenone emissions are usually characterized by broad and overlapping bands. In addition, the dependence of the green-band spectral shape on the film-preparation conditions is an indication of the likely presence of different origins for such emission features. Interestingly, it has been shown that complete or partial suppression^[19,20] of the green bands can be obtained by alteration of the polyfluorene chemical structure in ways that one would expect would affect significantly the formation of interchain excited species, and the 'spectral' diffusion of any excitation within the available density of states, but little or not at all the formation of fluorenone defects. Such structural alterations include: i) copolymerization with comonomers that disrupt chain planarity and reduce the conjugation length,^[15,21,22] ii) introduction of more sterically hindered side chains, iii) variation of the chain length at the C9 position of the fluorene unit,^[20,23] iv) an increase of the molecular weight of the polymer,^[24] and v) blending of the polyfluorene with hole-transport materials.^[25] Interestingly, red-shifted bands are not usually observed in cyclodextrin-threaded polyfluorene-based polyrotaxanes.^[26]

Here, we explore an alternative, and to our knowledge novel, approach to the suppression of green emission from polyfluorenes, that is based on the incorporation of twisted biphenyls in random copolymers with 9,9-dihexylfluorene (see Fig. 1 for the chemical structure). Such twisted biphenyl moieties modify the copolymer planarity, thus reducing close packing between chains and also the conjugation length, as confirmed by both theory and experiment.

2. Results and Discussion

Figures 2a–c, 3a–c, and 3d–f display, respectively, the absorption, photoluminescence (PL), and (EL) spectra of the oxepins, thiepins and azepins derivatives, as compared with the homopolymer. The EL properties of the polymer diodes are reported in Table 1.

To provide insight into the effect of substituting dibenzodihydroheteropins into the polyfluorene chains, quantum-chemical and molecular-mechanics calculations have been performed on model molecules. Oligomers consisting of 5–6 fluorene units were modelled and oxepin or thiepin sulfone monomers were systematically substituted into the chain to mimic increasing

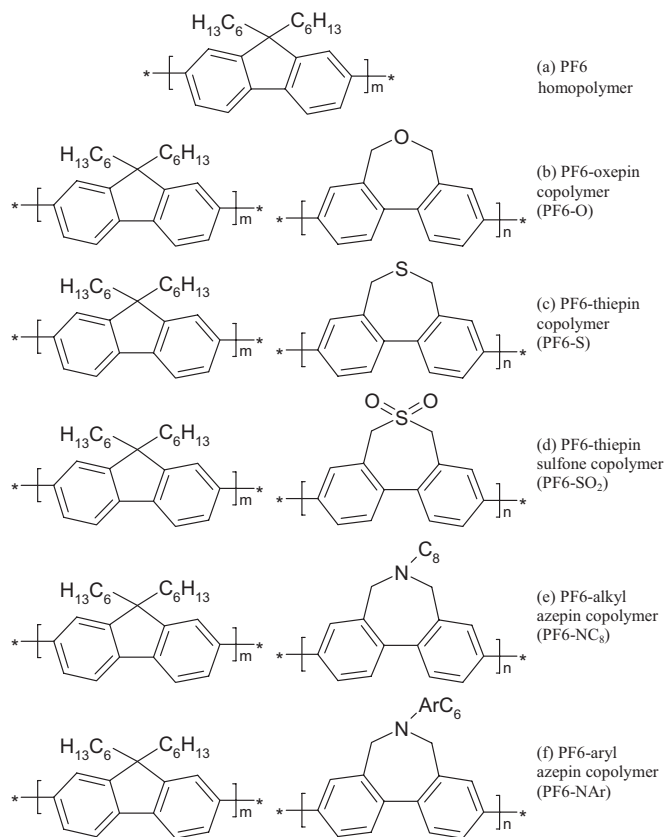


Figure 1. The chemical structures of the investigated materials: a) poly(9,9-dihexylfluorene), b) poly[(9,9-dihexylfluorene)-*co*-(5,7-dihydro-dibenz[*c,e*]oxepin)], c) poly[(9,9-dihexylfluorene)-*co*-(5,7-dihydro-dibenz[*c,e*]thiepin)], d) poly[(9,9-dihexylfluorene)-*co*-(5,7-dihydro-dibenz[*c,e*]thiepin sulfone)], e) poly[(9,9-dihexylfluorene)-*co*-(5,7-dihydro-*N*-octyl-dibenz[*c,e*]azepin)], and f) poly[(9,9-dihexylfluorene)-*co*-(5,7-dihydro-*N*-(4-hexylphenyl)-dibenz[*c,e*]azepin)].

comonomer content. Figures 4a,b report the calculated INDO/SCI (intermediate neglect of differential overlap Hamiltonian/single configuration interaction) singlet excited-state two-particle wavefunctions for a six-unit fluorene oligomer and the corresponding molecule substituted with two thiepin sulfone moieties.^[27] The calculated vertical transition wavelenghts, λ_{\max} , for absorption and emission also confirm that the energy gap is increasing upon oxepin and thiepin sulfone substitution into the fluorene chain.

Figure 5a shows the (force-field) optimized geometric structure of a single six-unit-long polyfluorene chain together with that of the corresponding oligomer including two oxepin units in the 2 and 5 positions. The most favorable interchain packing structure, as obtained at the molecular-mechanics level for a cluster of three six-unit fluorene oligomers, is displayed in Figure 5b. Figures 5c,d illustrate how the intermolecular distances vary as two fluorene units were substituted for two oxepin or thiepin sulfone units, respectively.

The intra-biphenyl torsion angles, as obtained from single-crystal X-ray spectroscopy for oxepin, thiepin, and thiepin sulfone, were found to be 41, 49, and 53°, respectively. This trend

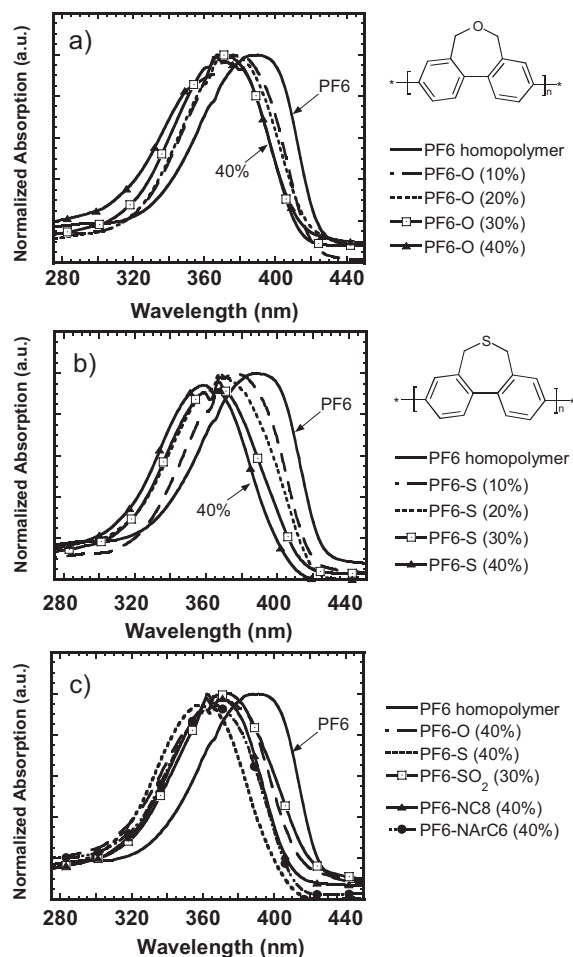


Figure 2. Normalized absorption spectra of 95 nm-thick polymers spin-cast on spectroil substrates of a) oxepin copolymers, b) thiepin copolymers, and c) the best copolymers (i.e., displaying the greatest green-emission suppression) from each series.

is well reproduced by the AM1 calculations (see Experimental), with computed twisting angles ranging from 42° for oxepin to 50° for thiepin sulfone.

Cyclic voltammetry (CV) data show that the highest occupied molecular orbital (HOMO) of the azepin copolymers is at ~5.5 eV below vacuum, whereas it is 5.7 eV below vacuum for PF6 and PF6-SO₂, and 5.8 eV below vacuum for PF6-S and PF6-O. The INDO calculations indicate a slight stabilization of the HOMO (increase in ionization potential), by typically ~0.2 eV, when switching from representative oligomers of the homopolymer to the corresponding model molecules for oxepin, thiepin, and thiepin sulfone copolymers.

The success of our strategy is demonstrated by the progressive shift of the absorption features in both the oxepins and the thiepins (Figs. 2a,b), and by the remarkable suppression of the previously mentioned green emission, both in the PL and EL spectra (Fig. 3). The progressive shift of the absorption profiles apparent in Figures 2a,b points to a reduction of the polymer conjugation via decrease of chain planarity and/or of the molecular strands close-packing. Interestingly, the slopes of the

spectra on the long-wavelength side with respect to the peak are smaller than for the homopolymer. This might be related to the increased disorder that is expected following the substitutions. In some cases we also observe some limited spectral broadening (e.g., the full width at half maximum of the oxepin-40% derivative is of ~71 nm, compared to ~66 nm for the homopolymer), but we prefer not to read too much into such data, since reduction of interchain interactions and packing is known to lead to a reduction of the absorption linewidth^[26] in the specific case of polyfluorenes. Such reduction, which could be greater than the broadening arising from increased disorder, significantly complicates the analysis. In addition, the absorption spectra were taken at room temperature, and their width is therefore significantly influenced by the excitation of various vibrational modes, which all contribute to the broadening. Such effects are likely to mask more subtle variations due to the change in conjugation.

The high-energy peaks at 420 nm and 450 nm in Figure 3, with distinguishable vibronic features, are attributed to the pristine chromophores. The differences between the PL and EL spectra are to be expected, owing to the energy-selective nature of charge-transport in organic semiconductors. We have also superimposed the PL and EL of the 40% thiepin containing copolymer (not shown), and found a close match of both spectra, suggesting that emission sites are similar in origin. We do not find the same level of green-emission suppression in aryl azepin copolymers, suggesting that the aryl ring enhances delocalization of electron density into the side groups, thus increasing conjugation.

Complete suppression of the green band in EL spectra from diodes incorporating Ca/Al cathodes is particularly remarkable in the light of the recent report that Ca catalyzes the formation of fluorenone defects.^[28] In fact, our diodes do not include any electron-injection layer capable of blocking calcium diffusion as reported by Gong and co-workers.^[28] This does not mean that defects are not formed or present in our materials, since although carbonyl features have not been detected in IR spectra of the pristine materials,^[29] their concentration may be below our detection threshold (~1%). We still have a lot of fluorene groups in the twisted copolymers and would therefore expect to have similar amounts of fluorenone groups in all our materials. Hence the green emission in the polyfluorene and its absence in the twisted materials would not be attributable to fluorenone groups.

The suppression of the green band can then be explained, even in the presence of ketone defects, by hindered diffusion of the generated excitons to the defective sites; the increased intermolecular separations associated with the twisted biphenyl moieties (vide infra) are indeed expected to lead to reduced exciton diffusion. The crucial point is that, irrespective of the mechanism responsible for green emission (interchain excited states or ketone defects), such red-shifted emission is suppressed, thus demonstrating the importance of the proposed functionalizations, and their expected effect on the polymer supramolecular organization, for the control of the solid-state photophysics.

Focusing more closely on the thiepin sulfones and azepin copolymers, and comparing the best (in terms of green band

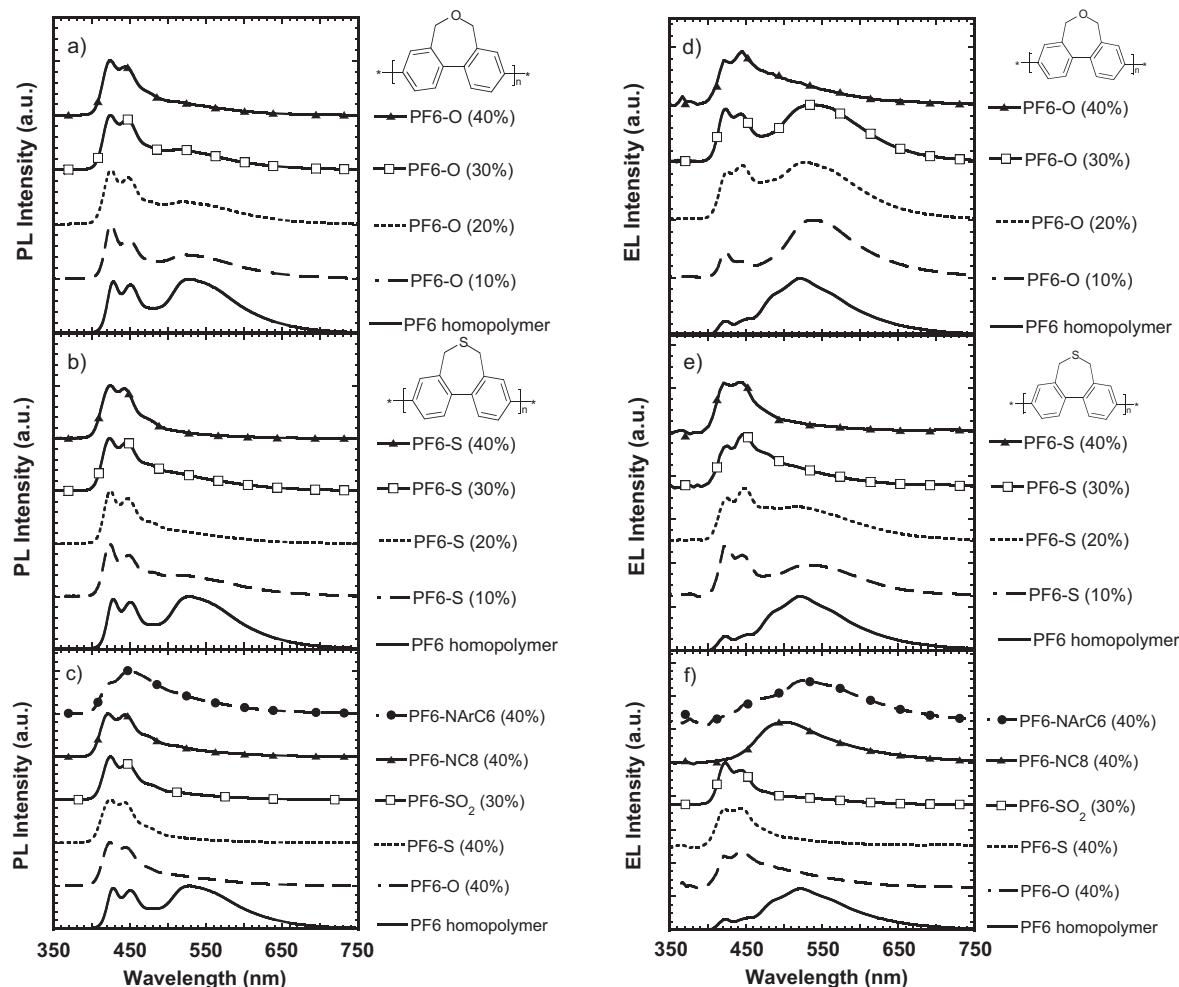


Figure 3. a–c) PL spectra of 95 nm thick polymers spin cast on spectrosil substrates excited with a 325 nm He–Cd laser beam in air within an integrating sphere: oxepin copolymers (a), thiepin copolymers (b), and the best copolymers from each series (c) (i.e., displaying the greatest green-emission suppression). d–f) EL spectra of copolymer devices, of configuration, ITO/PEDOT (40 nm)/polymer (95 nm)/Ca–Al, measured at 10^{-2} mbar: oxepin copolymers (d), thiepin copolymers (e), and the best copolymers from each series (f). The CIE coordinates, calculated using 1931 observer parameters, for EL emission from thiepin, thiepin sulfone, and oxepin copolymers are (0.19,0.13), (0.19,0.15), and (0.21,0.21), close to the accepted display color standard (PAL — phase alternating line) of (0.15,0.06) for blue.

Table 1. Electroluminescent properties of ITO/PEDOT (40 nm)/polymer (95 nm)/Ca–Al LEDs, for the best copolymers of each series, measured at 10^{-2} torr. The last column reports the PL efficiency of thin films of the materials spin-cast on spectrosil substrates. More work is needed to achieve a satisfactory explanation for the variation of the PL efficiency across the range of explored materials. However, we note that a hindered diffusion of excitons to defect sites, and therefore a higher efficiency, should be expected for the PF6 derivatives with respect to the homopolymer (as in the case of PF6-O and PF6-SO₂, and, to some extent of PF6-NC8).

Sample	Turn-on voltage [V]	Luminous efficiency [cd A^{-1}]	PL efficiency
PF6	10.8	0.51	0.2
PF6-O (40 %)	5.8	0.24	0.5
PF6-S (40 %)	11.3	0.03	0.05
PF6-SO ₂ (30 %)	4.4	0.09	0.5
PF6-NC8 (40 %)	16.3	0.01	0.25
PF6-NArC6	12.0	0.10	0.09

suppression) of each series in Figures 2c,3c,3f, we note that: i) the absorption peaks of all copolymers are blue-shifted with respect to the homopolymer; ii) in Figure 3c, all but one of the copolymers show a reduction in green emission and also a high-energy shift in the main blue emission for all copolymers; and iii) azepin-based copolymers are the only ones for which we have not been able to achieve blue emission.

Although emission characteristics are the most important for light-emitting diodes (LEDs), absorption spectra can also afford a wealth of information, and it is interesting to discuss them in the light of the intra-biphenyl torsion angles as determined via X-ray diffraction of model oligomers. From Figure 2c we see that the thiepin copolymer produces the most pronounced blue-shift, and that is consistent with the higher ring torsion angle of 48° in thiepin, compared to 42° for oxepin-based materials. The thiepin sulfone copolymer, character-

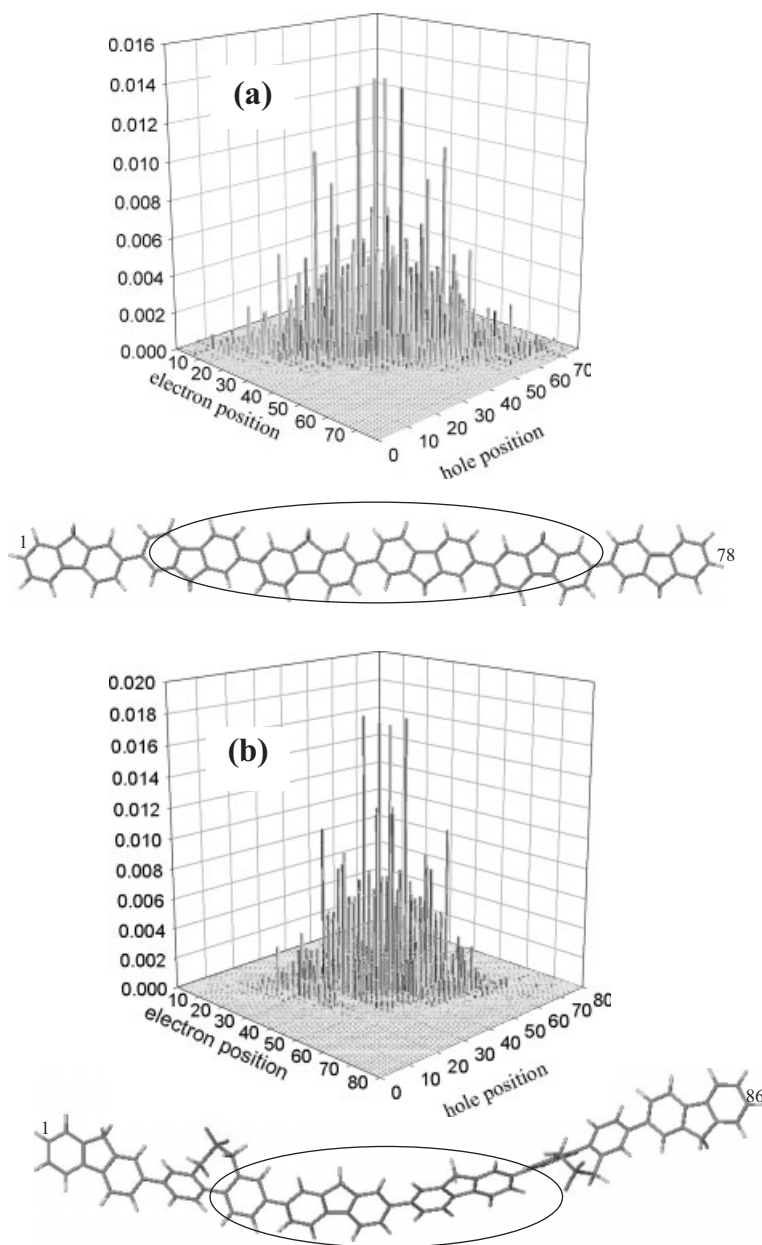


Figure 4. INDO/SCI electron-hole wavefunctions computed in the relaxed lowest singlet excited state for a) the six-unit fluorene oligomer and b) the corresponding molecule including two thiepin sulfone units in positions 2 and 5. The corresponding chemical structures are shown below the plots; the circled regions correspond to domains with highest occupation probabilities.

ized by the largest torsion angle of 54° , cannot be directly compared with the others because the twisted comonomer content is only 30%. The azepin copolymers, both PF6-NC8 and PF6-NArC6, also exhibit blue-shifted absorption peaks. These results reflect the bulkier pendant groups that introduce more disorder along the copolymer chain, so that intrachain conjugation length is reduced and chain packing is obstructed. Notably, the torsion angles are also consistent with the progression of the Commission Internationale de l'Eclairage (CIE) coordinates of the EL spectra of the 40% oxepin, 40% thiepin, and 30% thiepin sulfone copolymers of (0.21,0.21), (0.19,0.13), and

(0.19,0.15), that offer a quantitative description of the perceived colors (blue-green, blue, and purplish blue, respectively).

Further evidence of the ability of the dibenzodihydroheteropin-based copolymers to limit the π -delocalization and thus blue-shift the lowest optical transition is demonstrated by the calculated λ_{\max} values (Table 2). Since oligomer models were used in our calculations, the predicted absorption and emission electronic transitions are blue-shifted with respect to experiment. Nonetheless, increments in twisted biphenyl content result in blue-shifted absorption and emission spectra. The electron-hole excited-state wavefunctions (Fig. 4) confirm that introduction of heteropin within the polyfluorene chains squeezes the excitation over the unsubstituted fluorene domains. Geometric relaxation in the lowest excited state leads to a lowering of the inter-unit torsion angles, with values on the order of 40° in the ground state going down to $\sim 25^\circ$ in the lowest singlet excited state; such tendency towards a more planar structure in the excited state, hindered by the presence of heteropin units, confines the electronic excitations around the heteropin-free segments resulting in higher-lying optical transitions.

The influence of the nature of the bridging moieties on the supramolecular organization is illustrated in Figure 5, showing the force-field-optimized geometric structures of three-chain clusters formed by representative oligomers of the different materials. For the homopolymer the calculations indicate that a face-to-face arrangement, with the molecules rotated by 180° about their longitudinal axes to reduce steric repulsion between the bridging units and maximize π - π interactions, is a favourable stacking configuration (Fig. 5b). The incorporation of the highly twisted dibenzodihydroheteropins, however, leads to the formation of 'torsional kinks' along the chains, which adopt a zigzag shape, as visualized in Figure 5a. As a consequence, the chain packing in the copolymers is more loosely defined, with a smaller number of close intermolecular contacts and larger average interchain distances as compared to the homopolymer. In Figures 4c,d we further note that the thiepin sulfone-containing molecule, characterized by the largest torsion angle, also shows the largest interchain spacing. The theoretical study described above thus provides quantitative evidence that the biphenyl torsion angle controls the degree of *intrachain* conjugation and affects the relative *intermolecular* packing of the chains in the solid state. Large twisting angles along the polymer chains ensure high-energy optical transitions in the isolated molecules, *vide supra*, and reduce (or prevent) interchain interactions. As a result, green emission is effectively suppressed.

From CV we found that the HOMO of the azepin copolymers is at about 5.5 eV below vacuum (against 5.7 to 5.8 eV for the other materials), showing that, except for the azepin

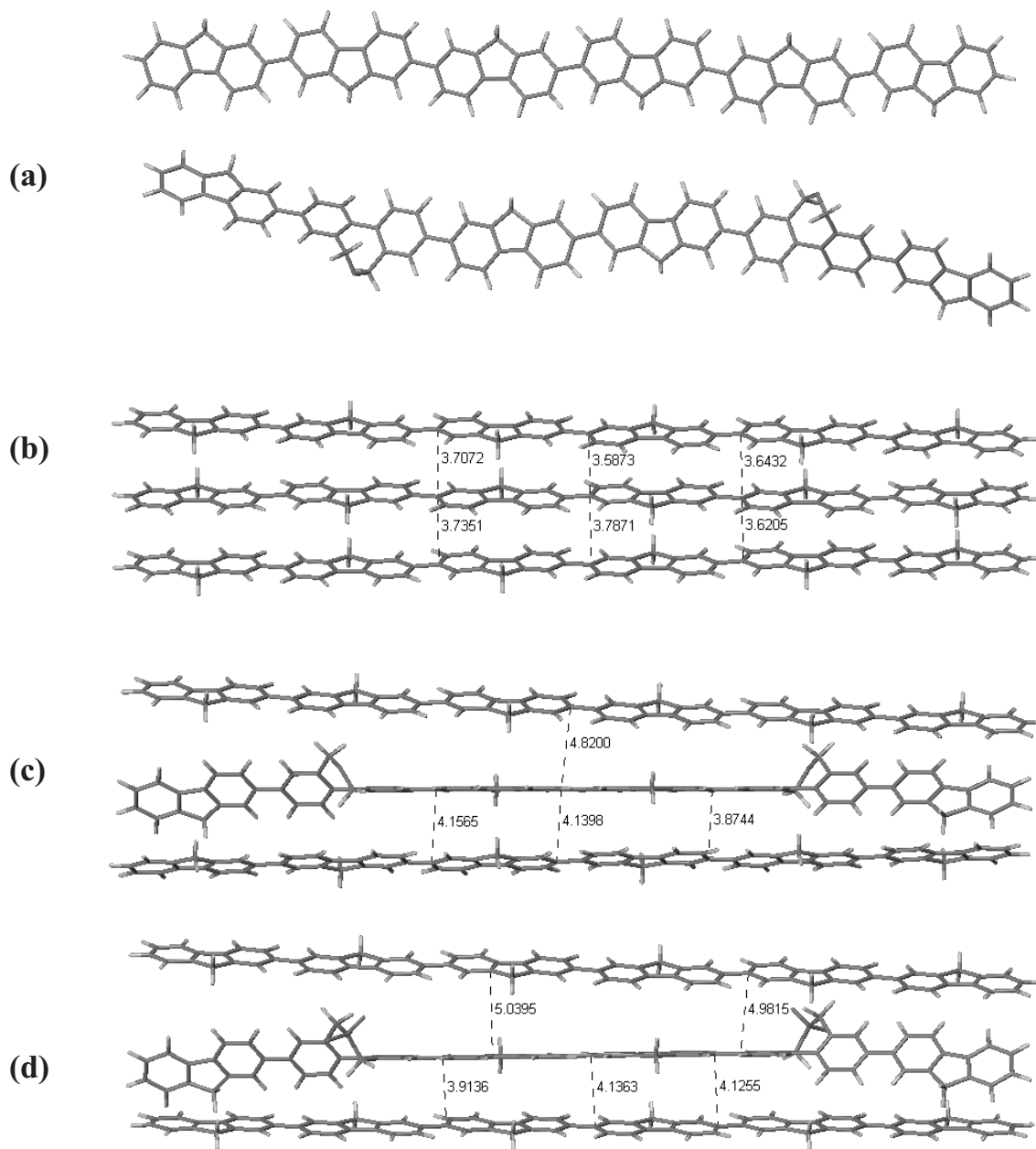


Figure 5. Force-field-optimized geometric structures of: single six-unit unsubstituted fluorene oligomer and the corresponding oligomer including oxepin units in positions 2 and 5 (a), three-molecule clusters built from six-unit-sized un-substituted fluorene oligomer (b), and the corresponding oligomers with oxepin units in 2,5 positions (c) and thiepin sulfone units in 2,5 positions (d). The intra-biphenyl torsion angles of oxepin, thiepin, and thiepin sulfone monomers determined from X-ray diffraction data on single crystals of oligomers are 42, 48, and 54°, respectively; the corresponding values are 42° for oxepin and 49° for thiepin sulfone at the AM1 level, 42° and 50° at the force-field level. For the sake of simplicity, the long alkyl chains have been substituted with hydrogens and the twisting angles between the repeating units fixed to zero in these simulations; the resulting geometric structures should therefore be considered solely at a qualitative level, as an indication of how the change in the nature of the bridging moieties perturbs the supramolecular organization.

groups, there is only a minor effect of the C9 functionalization on the electronic properties of the highest occupied orbital. This evolution is supported by the INDO calculations that indicate only a slight stabilization (by less than 0.2 eV) of the HOMO level upon incorporation of heteropin units, and suggests that the hole-injection barriers should not be dramatically different, with the exception of the azepin copolymers. It was

not possible to determine lowest unoccupied molecular orbital (LUMO) levels from reduction peaks, and we prefer not to read too much into what can be obtained by summing the value of the optical gap to the CV-determined HOMOs, because this may lead to substantial inaccuracies.^[30] Such an approximation is even more risky in our case, owing to different shapes of the absorption features, for the different materials, and to signifi-

Table 2. INDO/SCI vertical transition wavelengths (λ_{max}) as calculated from the ground-state (absorption) and excited-state (emission) optimized geometries of representative oligomers. (F)_n denotes a fluorene segment including *n* units. O and SO₂ represent oxepin and thiepin sulfone units, respectively.

Oligomer	Absorption wavelength (λ_{max}) [nm]	Emission wavelength (λ_{max}) [nm]
(F) ₆	376	412
(F) ₅	372	412
(F) ₄ -O-F	343	390
(F) ₃ -O-F	339	390
F-O-(F) ₂ -O-F	339	392
F-O-F-O-F	332	380
(F) ₄ -SO ₂ -F	343	390
(F) ₃ -SO ₂ -F	339	390
F-SO ₂ -(F) ₂ -SO ₂ -F	339	389
F-SO ₂ -F-SO ₂ -F	331	384

cant differences between the shifts of the absorption edges, and peaks. Nevertheless, since both absorption edge and peak are significantly red-shifted for the homopolymer, it appears that the electron injection should be sizeably smaller for such material (by ~0.2 eV) compared with the others. This hypothesis is confirmed by the INDO calculations for the oxepin- and thiepin-based copolymers, which show a destabilization of the LUMO (decrease in electron affinity) by ~0.3 eV with respect to the homopolymer. The effect is however reduced (~0.1 eV) for the thiepin sulfone derivatives, a feature that we attribute to the strong electron-withdrawing character of the sulfone groups.

The smaller electron-injection barrier may indeed be the reason for the higher EL efficiency of the PF6 with respect to the other copolymers, despite the fact that the PL efficiency is not the highest of the materials studied here. Although a full investigation of the electrical and EL properties of these different classes of materials is clearly beyond the scope of the work reported here, we can nevertheless extract two useful observations from our preliminary studies of the current–density and luminance versus voltage characteristics (Table 1). First, we find little correlation between the value of the torsion angles (and thus the intrinsic conjugation of the material) and the turn-on voltage. Second, the thiepin sulfone copolymer retains a low turn-on voltage at 4.4 V, despite a biphenyl torsion angle of 54°. As suggested by the calculations, this effect arises from the electron-withdrawing nature of the thienyl-S,S-dioxide moiety, which increases the electron affinity of the copolymer.^[31] We note that the structures we tested are standard, single-layer, LEDs which are not optimized in terms of electron injection at the cathodes,^[32] as demonstrated by the high turn-on voltages. Further optimization will require both determination of the LUMO positions, to select the best cathodes, and of the materials' mobilities, to determine how torsion angles influence intra- and interchain charge transport, and thus position and extent of the recombination region. In particular, we expect significant improvements in the external efficiency and lu-

minance upon insertion of suitable buffer layers between the active materials and the cathodes.

3. Conclusion

We have explored ways to prevent the degradation of the color purity of polyfluorene-based blue-emitting polymers, which is often compromised by 'long-wavelength' green emission bands, previously attributed either to polymer interchain species and/or to formation of emissive fluorenone defects. Our effort has concentrated on the characterization of a new class of polyfluorene derivatives that are modified by insertion of functional groups at the bridging points (position C9), so as to increase inter-ring torsion angles. We found that our approach was successful in suppressing the occurrence of the green emission bands in both photoluminescence and electroluminescence spectra of random copolymers of the modified polyfluorenes and the homopolymer. We also complemented our work with quantum-chemical calculations on model oligomers, to quantitatively address the influence of the bridging unit on the torsion angles, and the resulting excited-state properties. On the basis of our combined theoretical and experimental results we can conclude that an increase of intrabiphenyl torsion angles is a viable strategy for suppression of long-wavelength emission bands in polyfluorenes.

4. Experimental

The copolymers were synthesized by a modified Suzuki cross-coupling process following the work of Inbasekaran and co-workers [22]. A unique three-monomer system consisting of 2,7-dibromo-9,9-dihexylfluorene, 3,9-dibromo-5,7-dihydro-dibenz[2,8]oxepin (Fig. 1b), and 2,7-di(4,4,5,5-tetramethyl-1,3,2-dioxaboralane)-9,9-dihexylfluorene were polymerized in toluene, aqueous sodium carbonate, and Aliquat (*N*-methyl-*N,N*-dioctyl-1-octanaminium chloride, methyltricaprylammonium chloride, tricaprylmethylammonium chloride) under nitrogen ambient using tetrakis(triphenylphosphine)palladium(0) as catalyst. The resulting mixture was heated to 100 °C for 48 h. The polymer was precipitated in methanol and then purified by dissolving into toluene, filtered, and then re-precipitated into methanol. In this way, comonomers of 10 %, 20 %, 30 %, and 40 % were added to the resulting copolymers. Other copolymers were also synthesized with thiepins (Fig. 1c), thiepin sulfones (Fig. 1d), and azepins (Figs. 1e,f) as comonomers. Details of the synthesis will be reported elsewhere [33].

All optical investigations were carried out at room temperature on thin films prepared by spin-casting the (co)polymer solutions onto spectroscopic substrates. All absorption spectra of the films were measured with an HP 8453 spectrophotometer. Both PL and EL spectra were taken with an Oriel Instaspec charge-coupled device (CCD)-matrix spectrograph. For the EL experiments we used commercially available indium tin oxide (ITO)-coated glass (Asahi), which was cleaned (15 min) in an ultrasonic bath with acetone and isopropanol, and after drying in a flow of nitrogen, treated with an oxygen plasma (250 W, 10⁻² mbar, 10 min) [34]. The substrates were then spin-coated with a 100 nm-thick film of poly(ethylene dioxythiophene)/poly(styrene sulfonic acid), PEDOT:PSS (HC STARCK), later baked at 200 °C for one hour under nitrogen flow in a fume hood. The LEDs were completed by spin-coating the active polymer, and thermally evaporating a Ca/Al cathode at 10⁻⁶ mbar. The EL (at 10⁻² mbar) was measured using a calibrated large-area silicon photodiode.

The geometries of the molecules in their ground state and lowest singlet excited state were optimized by means of the semiempirical Har-

tree-Fock Austin Model 1 (AM1) method [35], as implemented in the AMPAC package [36]. These geometries were then injected into INDO/SCI [37] calculations of the singlet–singlet vertical transition energies and oscillator strengths. No attempt has been made here to reproduce the vibrational progression seen in the experimental optical spectra; a detailed analysis of the vibrational modes coupled to electronic excitations will be reported elsewhere. The influence on molecular packing of introducing twisted biphenyl moieties along the polymer chains has been gauged at the molecular mechanics level (using the polymer-consistent force field (PCFF) [38]) on small molecular clusters. Note that for the sake of simplicity, the torsion angles between the repeating units have all been frozen to zero in these force-field calculations (this is a reasonable approximation in the solid state where packing interactions drive the structures towards planarity).

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