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# Bigger and Brighter Fluorenes: Facile π-Expansion, Brilliant Emission and Sensing of Nitroaromatics

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Dedication ((optional))

**Abstract:**  $\pi$ -Expanded butterfly-like two-dimensional (2D) fluorenes and three-dimensional (3D) spirobifluorenes **1-5** were synthesized via oxidative cyclization strategy with a high regioselectivity. Through structural modification via  $\pi$ -expansion, it was possible to achieve near-ultraviolet absorption, bright-blue emission, very high close-tounity fluorescence quantum yields in solution as well as in film states, and deep-lying HOMO energy levels with excellent thermal stabilities. Further, these electron-rich compounds revealed notable behaviour towards sensing of nitroaromatic explosives, such as, picric acid, up to a detection limit of 0.2 ppb.

In recent years, organic luminescent materials have emerged as inextricable materials for application in organic light emitting diodes (OLEDs),<sup>[1a]</sup> organic light emitting transistors (OLETs),<sup>[1b]</sup> light emitting electrochemical cells (LEECs),<sup>[1c]</sup> solid-state lasing and sensing,<sup>[1d,e]</sup> and in bio-imaging,<sup>[1d]</sup> etc.<sup>[1]</sup> In particular, fluorenes their derivatives. oligofluorenes and and spirobifluorenes have been shown to exhibit excellent fluorescence behaviour, both in solution and film/solid states.<sup>[2]</sup> Advantageously, fluorene-based compounds possess high thermal stability, good processability (via dialkyl substitution at the 9-position), and ready availability. However, their huge band gaps and deep highest occupied molecular orbital (HOMO) energy levels are limiting factors to a considerable extent for their effective utilization as functional materials. It may be partly originated from the unique structural attribute of fluorene.

As such, fluorene is a simple planar, rigid molecule with a methylene bridge that connects the 2,2'-positions of the biphenyl leading to a slightly bent geometry (162°) of banana-type. It is interesting to note that, though planar, the emission spectrum of simple fluorene ( $\lambda_{em}$  in cyclohexane = 306 (sh), 315 nm) highlights a significant blue-shift when compared to that of the parent biphenylene ( $\lambda_{em}$  in cyclohexane = 324, 330 (sh) nm) whose tilt angle due to the sterics imparted by ortho hydrogens of the phenyls is ca. 45° (Figure 1).<sup>[3]</sup> Because of their emission in the ultra-violet region, simple fluorenes/fluorene derivatives have not been investigated so far for sensor applications. In contrast, electrospun nanofibres, membranes and films, and polymer nanoparticles of poly(fluorenes) have been utilized for sensing purposes due to their long range exciton migration pathway and better electronic communication with the analytes.<sup>[4]</sup> Generally, synthesis of polymers suffers from batchto-batch variation, reproducibility and tedious purification. On the

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other hand, small molecule-based approaches<sup>[5]</sup> is promising in terms of direct synthesis, easy purification, better reproducibility and high fluorescence quantum yields. These advantageous properties associated with small molecules spurred our interest on the development of fluorenes as suitable candidates for sensor applications. Several electron rich simple, small-molecule polycyclic aromatic hydroarbons (PAHs), such as, pyrene,<sup>[6]</sup> triphenylene,<sup>[7]</sup> truxene,<sup>[8]</sup> fluoanthrene,<sup>[9]</sup> pentiptycene,<sup>[10]</sup> hexabenzocoronene,<sup>[11]</sup> etc. have been attempted for the detection of nitroaromatic compounds, due to favourable donor-acceptor interactions.<sup>[6-11]</sup>

Hence, to tap the fullest potential of the small less-explored fluorene skeleton (molecular length and width ca. 0.69 and 0.37 nm, respectively) for sensing applications, appropriate structural modification is essential. Structural modification so as to improve the optical and electronic characteristics via *extension* of the  $\pi$ -conjugation of fluorene is commonly accomplished either through its 2,7- or 3,6-positions,<sup>[12]</sup> but a least attention is devoted on the approach through *expansion* of the  $\pi$ -system of fluorene. We surmised,  $\pi$ -expansion, which leads to a larger skeleton with extensive  $\pi$ -delocalization, could be an attractive strategy to influence upon the electronic as well as optical behaviour of fluorenes, especially the photoluminescence quantum yields (PLQEs) and sensitivity of detection.

One of the ways to expand the  $\pi$ -system of fluorene is by annulation with aromatic or heteroaromatic units at the 2,3 and 6,7-faces (Figure 1). This would lead to a larger, planar, rigid, conjugated and electron-rich fluorene system which may have better optoelectronic properties. It is understandable that annulation at other faces of fluorene may lead to  $\pi$ -expanded fluorenes with non-planar geometry (helicenes) and limited conjugation, due to steric reasons.<sup>[13]</sup> Initially, Mullen's group have successfully exploited the most popular method-Scholl cyclization (Clar's method), i.e., oxidative cyclization strategy-to form  $\pi$ -expanded various 2D graphene-type architectures,<sup>[14]</sup> including "super-fluorenes" that possess limited solubility.<sup>[15]</sup> Later, Müllen et al. have synthesized n-type phthalimide fused one-dimensional (1D) fluorene derivatives and demonstrated their field-effect transistor (FET) behaviour.<sup>[16]</sup> Recently, Cheng's group have reported fluorenes fused with heteroaromatic thiophene and selenophene units to generate a new class of 1D pentacyclic dithienofluorene (DTF) and diselenofluorene (DSF) derivatives via sulphur-mediated thermal cyclization for better optoelectronic properties;<sup>[17]</sup> however, photoluminecsnece (PL) as well as the sensing behaviour of any of the above set of fluorenes have not been explored.<sup>[15,16,17]</sup> In the latter instances,  $\pi$ -expansion via ring-annulation/fusion at the 2,3 and 6,7-faces of fluorene was accomplished essentially by prior introduction of the right functional groups, such as, halogens, alkyls, etc., at the 2,3 and 6,7 positions. From this, it is clear that effecting multiple substitutions simultaneously at all the 2,3,6 and 7 positions of fluorene is challenging, tedious and involves several steps.<sup>[18]</sup>As

discussed earlier, fluorenes can be functionalized at 2,7 or 3,6 positions very readily.

Herein, we report the synthesis of m-expanded soluble 2D fluorenes/3D spirobifluorenes (1-5, Figure 1) starting from the readily obtainable 2,7-disubstituted fluorenes/spirobifluorenes via oxidative cyclization strategy under DDQ/MeSO<sub>3</sub>H conditions; the design of 2D (planar) and 3D (orthogonal)  $\pi$ expanded electron-rich fluorenes was aimed at tweaking the solution/solid state PL properties of fluorenes which in turn may be beneficial for effective sensing of nitroaromatics. Through  $\pi$ expansion, we have structurally enlarged fluorenes (molecular length, ca. 1.71 nm and width, ca. 0.78 nm, as deduced from Xray structural analysis) introducing extensive delocalization to achieve (i) absorption in the near-ultraviolet region (ca. 390 nm), (ii) very high PLQEs in solution (close to unity) as well as in film (up to 0.88) states, (iii) very good thermal stabilities (ca. 540 °C), and (iv) better optical band-gaps (~ 3.1 eV) with deep HOMOs (as low as -5.80 eV). These electron-rich bigger and brighter butterfly-like fluorene skeletons have been shown to act as excellent fluorescent sensors for nitroaromatic explosives with a detection limit upto 0.2-2.0 ppb.

Our synthetic approach to achieve target fluorenes **1-5** is shown in Scheme 1. Initially, we prepared the desired key intermediates—9,9-dihexyl-2,7-dibromofluorene **1k**,<sup>[19a]</sup> 9,9-diphenyl-2,7-dibromofluorene **2k**<sup>[19b]</sup> and 2,2',7,7'-tetrabromospirobifluorene **4k**<sup>[19c]</sup>—by modified literature procedures, cf. SI.<sup>[19]</sup> The dibromofluorene derivatives (**1k** and **2k**) and commercially purchased 2,7-dibromospirobifluorene **3k** 



Figure 1. Chemical structures of target  $\pi$ -expanded 2D fluorenes 1-3 and 3D spirobifluorenes 4-5.

were subjected to Pd(0) catalyzed two-fold Suzuki cross coupling reaction with biphenyl-2-boronic acid pinacol ester to produce the precursors in reasonably good yields (Scheme 1):

**1p**: 79% (R = C<sub>6</sub>H<sub>13</sub>), **2p**: 75% (R = Ph) and **3p**: 80% (R = spiro(2,2'-biphenyl)). Similarly, 2,2',7,7'-tetrabromospirobifluorene **4k**<sup>19c</sup> was subjected to four-fold Suzuki cross-coupling reaction with excess of biphenyl-2-boronic acid pinacol ester to deliver **4p** in 60% yield (Scheme 1).



**Scheme 1.** (a) Biphenyl-2-boronic acid pinacol ester, Pd(PPh<sub>3</sub>)<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, toluene:ethanol (3:1), 90 °C, 12 h for **1p**: 79%; 24 h for **2p**: 75%; **3p**: 80%, and **4p**: 60%.

Having obtained the precursors 1-4p in hand, we next targeted the π-expanded derivatives of fluorene (2D) and spirobifluorene (3D) systems 1-5. The biphenyl units in compounds 1-4p are appropriately placed for the structural  $\pi$ -elaboration of fluorenes by oxidative cyclization strategy. Generally, oxidative Scholl cyclization reactions can be carried out by a variety of oxidizing agents, viz., CuCl<sub>2</sub>, Cu(OTf)<sub>2</sub> and AlCl<sub>3</sub>, MoCl<sub>5</sub>, FeCl<sub>3</sub>, SbCl<sub>5</sub>, PIFA, DDQ/MeSO<sub>3</sub>H, etc.<sup>[20]</sup> Our initial attempts were with the most popular reagent, FeCI<sub>3</sub>.<sup>[21]</sup> When compound 1p was subjected to oxidative cyclization condition in presence of FeCl<sub>3</sub>, we observed the formation of a novel undesired ring chlorinated product 3, but not the dicylized product 1, in a regioselective fashion within 10 min (86% yield, Scheme 2). Compound 3 was thoroughly characterized, and X-ray crystal structure analysis of single crystals of 3 grown from chloroform or toluene solutions unequivocally confirmed that it is a trichlorinated derivative (Scheme 2) possessing rigid, coplanar structure with extensive  $\pi$ -conjugation (see SI for structural details). Such regioselectivity in oxidative cyclization reactions in presence of FeCl<sub>3</sub>, has been observed earlier.  $\ensuremath{^{[22]}}$  Also, ring chlorination has been observed as one of the major side reactions. besides oligomerization/polymerization, during oxidative cyclization reaction with FeCl<sub>3</sub>.<sup>[23]</sup> It is generally overcome by introducing stable blocking groups at the active positions of the starting material.<sup>[24]</sup> Several optimizations performed on the above reaction, viz., reducing FeCl<sub>3</sub> equivalents, reaction time, varying concentration of the reaction medium, bubbling the reaction mixture with nitrogen gas to remove the dissolved HCI, etc., to obtain 1 were not successful. To the best of our knowledge, 3

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serves as the first structural evidence for the chlorinated product obtained from the oxidative cyclization reaction of fluorenes. The pattern of substitution of chlorine atoms on the aromatic ring may provide valuable information about the mechanism of formation of such chlorinated products in Scholl reaction. In view of the beneficial use of chlorine in polycyclic aromatics, that provides effective molecular packing, we believe these candidates are of prominence in organic electronics.<sup>[25]</sup>





Scheme 3. (a) DDQ, DCM:MeSO₃H (10:1), 0 °C to rt, 2.5 h, 1: 76%; 12 h, 2: 60%; 5 h, 4: 75%; 6 h, 5: 73%.

Scheme 2. (a) FeCl<sub>3</sub>, DCM, rt, 10 min, 86%.

To avoid ring chlorination and achieve the target compound 1. we followed Rathore's oxidative cyclization strategy using DDQ/MeSO<sub>3</sub>H<sup>[26]</sup> with 1-4p that contain no blocking groups. At first, we optimized the reaction conditions with 1p. To our gratification, we observed complete dicyclization (1, 100% conversion) regioselectively in 1-2 h, when 4.0-5.0 equivalents of DDQ were used. Using the above optimized conditions, compounds 2 (76%) and 4 (60%) were synthesized in very good yields (Scheme 3). Under similar conditions (DDQ, 16.0 equiv.), the tetracyclized compound 5 was obtained in 73% yield (Scheme 3). It is important to note that the oxidative cyclization using 2-biphenyls at 2 and 7 positions of fluorene (1-4p), as above, is always observed to be regioselective, i.e., cyclization occurs only at 3 and 6 positions of fluorene. Aryl fusion at 1,2 and 7,8 faces of fluorene leading to a symmetrical regioisomer as well as 1,2 and 6,7 faces of fluorene leading to a cross one were not observed at all under the above experimental conditions (SI). Thus, the above method of achieving  $\pi$ expansion in fluorenes starting from 2,7-disubstituted derivatives is more advantageous than starting from 2,3,6 and 7 tetrasubstituted derivatives. As expected, compounds 1-5 exhibit excellent solubility in common organic solvents, such as chloroform, dichloromethane, tetrahydrofuran, ethyl acetate, toluene, chlorobenzene, dichlorobenzene, etc. All the starting materials, intermediates and final compounds were thoroughly characterized by infra-red, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic data, and high resolution mass spectrometry (see SI for details).

To examine the influence of  $\pi$ -expansion on the optical properties of fluorene, UV-vis absorption and photoluminescence spectrum of the  $\pi$ -expanded fluorene derivatives **1-5** were examined in dilute toluene solutions (ca. 1 × 10<sup>-5</sup> M) at room temperature. The UV-vis absorption spectral profiles of compounds **1-5** (Figure 2) display typical vibronic features similar to those observed for rigid coplanar polycyclic

aromatic hydrocarbons (PAHs).[27] This is in excellent agreement with the rigid and near-planar (tilt angle, ca. 3.36°) structure observed by 3 from X-ray structural analysis. All of them reveal a low energy absorption band corresponding to  $\pi$ - $\pi$ \* transition in the range of 375-380 nm, in addition to the high energy absorption bands at ca. 285 nm (not shown in Figure 2) and at ca. 344 nm (Table 1).<sup>[28]</sup> While substitution of diphenyl (as in 2, log  $\varepsilon$  = 4.50) and chlorine atoms (as in **3**, log  $\varepsilon$  = 4.79) red-shifts the absorption maximum by 2-6 nm when compared to that of the dihexyl derivative (as in 1, log  $\varepsilon$  = 5.01), we observe only marginal differences in the absorption spectrum when we move from  $2 \rightarrow 4 \rightarrow 5$  (2D $\rightarrow$ 3D). The inductive effect due to the ring chlorine atoms and the effect of substituents at the 9-position in the absorption spectrum is noteworthy here. It is notable that the absorption spectrum of 2 reveals a tail at around 400 nm, while such a feature is absent in other derivatives. A UV-vis absorption spectrum recorded at 80-90 °C in toluene with same concentration, indicated that it is an inherent molecular absorbance and not due to aggregation. This further signifies the role of diphenyl substituents in suppressing molecular aggregation. Interestingly,  $\pi$ -expansion in all the derivatives contributes to shifting the absorption maximum close to the visible region with absorption tailing all the way into the visible region; for comparison,  $\lambda_{max}$  (abs) of triphenylene in methanol is ca. 247 nm,  $^{[3]}$   $\lambda_{max}$  (abs) of fluorene in CHCl\_3 is ca. 300 nm  $^{[28]}$ and  $\lambda_{max}$  (abs) of DTF/DSF in CHCl<sub>3</sub> is ca. 340 nm.<sup>[17]</sup> To see, if the molecular properties (solution) of 1-5 are preserved in films, we carried out absorption spectral studies in a inert polymer, polystyrene (ps), matrix.<sup>[29]</sup> The absorption spectrum of ps films of 1-5 (0.1 wt%) exhibited a very similar behaviour to their solutions in toluene; notably, 2 exhibited a slight bathochromic shift (2-9 nm) when compared to other fluorenes (SI). This indicates that the intermolecular interactions are quite similar in both solution and film states under the above experimental conditions.

Table 1. Optical, electrochemical and thermal properties of $\pi$ -expanded 2D fluorenes 1-3 and 3D spir	obifluorenes 4 and 5.
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Compound	$\lambda_{max}$ abs (nm)/log $\epsilon$ (M <sup>-1</sup> cm <sup>-1</sup> ) at 379 nm	$E_9^{[b]}$	$\lambda_{max}$ em (nm) at $\lambda_{exc}$ = 342 nm		PLQE <sup>[d]</sup>	τ <sup>[a]</sup>	HOMO <sup>[e]</sup> LUMO <sup>[f]</sup>		$\mathcal{T}_{d}^{[g]}$
	soln <sup>[a]</sup>	(eV)	soln <sup>[a]</sup>	ps film <sup>[c]</sup>	soln/film	(ns)	(eV)	(eV)	(°C)
1	342, 357, 375/5.01	3.18	380, 400, 422	378, 400, 426	1.00/0.70	2.19	-5.76	-2.57	406
2	344, 360, 378/4.50	3.17	381, 403, 424	381, 403, 427	0.95/0.78	2.57	-5.82	-2.65	434
3	348, 356, 379/4.79	3.12	389, 405, 430	386, 406, 415	0.04/0.35	0.21, 1.85	-5.85	-2.73	412
4	344, 360, 379/4.64	3.15	382, 402, 425	381, 403, 426	0.84/0.86	2.59	-5.80	-2.65	456
5	344, 361, 380/4.91	3.13	384, 404, 424	383, 405, 429	0.78/0.88	2.72	-5.79	-2.66	542

[a] Measured from toluene solutions. [b] Optical band gap derived from the onset of absorption. [c] Measured from ps films. [d] Measured from toluene solutions using anthracene in ethanol ( $\Phi = 0.28$ ) as the standard,<sup>[30]</sup> and for films, diphenylanthracene in ps films ( $\Phi = 0.98$ ) is used as the reference;<sup>[31]</sup>  $\lambda_{exc} = 342$  nm, error <5%. [e] Calculated from cyclic voltammetry using dichloromethane solutions of **1-5** (1.0 mM) and 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> as the supporting electrolyte using the relation  $E_{HOMO} = -(E_{ox}-E_{[Fc_{VF}Fc_{}]} + 4.8)$  eV. [f] Calculated from the optical band gap and HOMO energy level using the relation  $E_{LUMO} = E_{HOMO} + E_g$  eV. [g]  $T_d$ -thermal decomposition temperature at 5% weight loss.



**Figure 2.** UV-vis absorption (left) and photoluminescence (right) spectra of **1-5** in toluene solutions. Inset: Photographs of toluene solutions and polystyrene films of **1-5** under room light (top) and under UV light ( $\lambda_{exc} = 365$  nm, bottom).

The optical band gap values derived from the onset of the absorption spectrum of films of **1-5** (Table 1) highlights a wide band gap energy (ca. 3.1–3.2 eV) attesting to their semiconducting nature. The band gap values obtained here are similar to tricyclic fluorene (truxene ca. 3.1 eV)<sup>[32]</sup> or much smaller than those of DTF/DSF derivatives (ca. 3.61 eV) reported earlier,<sup>[17]</sup> indicative of the extensive  $\pi$ -delocalization in these systems. Such wide band gap materials with brilliant blue emission are useful in white light generation with suitable dopants via fluorescence resonance energy transfer (FRET) mechanisms in OLEDs.<sup>[33]</sup>

As mentioned, 9,9-dialkylfluorenes are highly fluorescent compounds, and spirobifluorenes that possess orthogonal planes exhibit excellent fluorescence emission in the solid/film state. Compounds characterized by orthogonal planes are known to impede self-quenching mechanisms due to approach problems for aggregation.<sup>[34]</sup> The fluorescence quantum yields of compounds **1-5** were determined in toluene solutions (ca. 1 x  $10^{-6}$  M) and in inert polystyrene films in order to understand their fluorescence behaviour. As shown in Figure 2, all compounds **1-5** (in both solution and films) emit in the blue region (380–430 nm), which is characteristic of fluorenes. While the emission spectrum or peak positions do not change significantly, one may notice a considerable modification in the trend with PLQEs,

when we move from 2D to 3D. The compound 1 exhibited the highest PLQE of unity in the solution state with the following order for others: 1>2>4>5>3 (Table 1). It appears that expansion of the  $\pi$ -system of fluorenes (as in 1-5) enhances the luminescence efficiencies (up to ca. 32-40%) in solution, but does not affect the same; for comparison,  $\Phi$  (fluorene, EtOH) = 0.68 and  $\Phi$  (triphenylene, EtOH) = 0.60.<sup>[35]</sup> It is noteworthy to mention here that the PLQEs measured for helical fluorenes or helical sila-fluorenes or helical bitriphenylenes (arenes fused at 3,4 and 5,6 faces of fluorenes) are ca. 60-80% lower than that of the present fluorene system.<sup>[13]</sup> Usually, compounds with larger  $\pi$ -system tend to aggregate resulting in diminished PLQEs (aggregation-caused quenching, ACQ).[27] A molecular design (π-expansion with appropriate substituents at the methylene position), as shown above, paves way for fluorenes with stable blue emission and improved luminescence properties to serve as potential candidates in optoelectronic applications. The lowest PLQE observed with the trichloro compound 3 may be attributed to the enhanced non-radiative decay pathways probably caused by the chlorine atoms. In ps films, the PLQE order is as follows: 5>4>2>1>3; the spirocompounds 4 and 5 exhibit higher PLQEs than planar fluorenes 1-3 (Table 1). It is noteworthy that PLQE of films of 4 remains almost the same as that of the one in solution, while 5 improves drastically. It is evident that the spiro-configuration in 5, due to its unique orthogonal planes, clearly reduces intermolecular interactions impeding self-quenching, even after  $\pi$ -expansion.<sup>[36]</sup> The improvement of PLQE of 3 in the ps film (when compared to that in solution) could probably be attributed to the restricted motions, and hence reduced non-radiative decay pathways.<sup>[37]</sup> Further, studies on the PL lifetimes (Table 1) reveal a single exponential decay (ns) for compounds other than 3, which probably is due to different excited state species arising from the polarity variation caused in its excited states.<sup>[38]</sup> Indeed,  $\pi$ -expansion, rigidity and planarity of these new fluorenes, and the orthogonal nature of spirobifluorenes improve the emission (blue) characteristics without hampering the PLQEs. The near unity PLQEs (1) achieved in solution as well as a PLQE of 0.90 (5) in a ps film is

one of the highest for any compound reported in fluorene/spirobifluorene series (for comparison chart, see SI).

In order to understand the effect of  $\pi$ -expansion and introduction of spiro-units on the thermal properties of compounds 1-5, and to gauge their functional utility in thin-film devices, thermal stabilities of 1-5 were estimated by thermogravimetric analyses (TGA). All these compounds 1-5 were found to exhibit extraordinary thermal stabilities (Table 1); thermal decomposition temperatures ( $T_d$ ) of **1-5** are greater than 400 °C with maximum (542 °C) being exhibited by 5. This may be readily discernible from the rigid, planar, π-expanded fluorene/spiroconnected bifluorene unit.<sup>[34]</sup> In addition, the thermal stability trend, 5<4<2<3<1, suggests, (i) longer alkyl chains decrease thermal stability (due to their flexible thermal motions), (ii) substitution of alkyl to aryl to spiro substituents at the methylene carbon bridge increases the thermal stability, (iii) incorporation of chlorine atoms into the skeleton (as in 3) indeed improves the thermal stability.

Having developed  $\pi$ -rich fluorenes with excellent optical and thermal characteristics, the electron donor tendency of these polycyclic aromatic hydrocarbons (PAHs) were novel investigated for their utility as sensors. The HOMO and LUMO energy levels of the newly synthesized compounds 1-5 were extracted from cyclic voltammetry (CV) experiment in dichloromethane (Figure 3a) solutions. Compounds 1-5 displayed only reversible one electron oxidation potentials in support of their electron rich/donor nature. The HOMO energy levels calculated from the differential pulse voltammogram (DPV) are -5.76 (1), -5.82 (2), -5.85 (3), -5.80 (4), and -5.79 (5) eV, and the LUMO energy levels were derived from the corresponding optical band-gap  $(E_g)$  values and the HOMO energy levels (Table 1). The HOMO energy levels of 2-5 are slightly deeper (ca. 0.16-0.25 eV) than those of the previously reported thiophene/selenophene-fused fluorenes (-5.60 to -5.75 eV),<sup>[17]</sup> besides lowering of the LUMO energy levels (ca. 0.5-0.7 eV), which showcases the effect of extended  $\pi$ -conjugation as well as the air-stability gained by these systems.[39] We postulated that the donor ability (better oxidizing behaviour) arising from the delocalized  $\pi^{*}$  excited state would facilitate exciton delocalization (lifetime) which in turn might increase the electrostatic interaction between the donor fluorophore and electron deficient nitroaromatic analyte. In addition, the wellpositioned LUMO energy levels of the fluorophores may facilitate photo-induced electron transfer (PET) to the electron poor aromatic analytes (Figure 3b).



Figure 3. a) Cyclic voltammograms of 1, 3 and 5 recorded in dichloromethane solution. b) Possibility of photoinduced electron transfer in 2 and 4 upon titration with DNT and PA.

Various electron-rich PAHs have been attempted for the detection of nitroaromatic compounds.<sup>[5,6-11,40]</sup> The highly sensitive and explosive nature, and very low vapour pressure (5.8 × 10<sup>9</sup> Torr at 25 °C)<sup>[40b]</sup> of PA, when compared to other nitrophenols and TNT, especially, make it an important and challenging candidate for detection which warrants development of efficient sensors. As mentioned earlier, fluorenes and their analogues have not been tested as sensors for nitroaromatics (NAs), since most of them emit in the UV-region. The excellent fluorescent properties (as evidenced by very high PLQEs) as well as the improved donor behaviour (as evidenced by their oxidation curves in cyclic voltammetry) exhibited by the new set of structurally modified fluorenes 1-5, herein prompted us to explore their functional utility further as sensors for the detection of electron-deficient nitroaromatics (explosives), such as, picric acid (PA), 2,4-dinitrophenol (DNP), p-nitrophenol (PNP), phenol (P), 2,4-dinitrotoluene (DNT), p-nitrotoluene (PNT), and nitrobenzene (NB). The quenching experiments were conducted on 2D fluorene 2 and 3D fluorenes 4, as representative cases. As expected, titration experiments of 2D fluorene 2 and 3D fluorene 4 with all the nitroaromatics exhibited fluorescence quenching to a greater extent without change in emission profile and energy (SI). The quenching of fluorescence was found to be negligible for other electron deficient aromatics, such as, dichlorobenzene (CB), benzoic acid (BA), etc., and phenol (see, SI). Interestingly, quenching was found to be significant in the case of p-quinone (Q). The Figure 4a typically reveals a decrease in fluorescence intensity of 2 (1  $\times$  10<sup>-6</sup> M, toluene) upon addition of varying amounts of PA (1 mM) in toluene solution; about 74% PL quenching was observed upon addition of 200 equivalents of PA. Under the above conditions, the spiroconfigured 4 revealed a similar PL quenching behaviour (ca. 72%), but 5 revealed a marginal increase in its response (ca. 79%). The quenching of fluorescence in both the cases were easily detected by a naked eye upon UV light ( $\lambda_{exc}$  = 365 nm) illumination.

The Stern-Volmer (SV) curves were generated by plotting the change in fluorescence intensity of the fluorophore against concentration of the quenchers added.<sup>[41]</sup> Indeed, in all cases, at lower concentrations (0.15-0.20 mM), the SV plots were found to be linear, but adapted a hyperbolic behaviour at higher concentration of the quenchers. This suggests an involvement of both static and dynamic quenching behaviour at higher concentration of the analytes.[42] Hence, the Stern-Volmer constants ( $K_{sv}$ ) for compounds 2, 4 and 5 were derived from the linear regime (up to ca. 0.2 mM) and were found to be 9.59  $\times$ 10<sup>3</sup> M<sup>-1</sup>, 11.9 × 10<sup>3</sup> M<sup>-1</sup> and 12.6 × 10<sup>3</sup> M<sup>-1</sup>, respectively, for PA (Figure 4b). These values suggest that the sensitivity of 5 is relatively better, and they are in good agreement with other PAHs carrying no substituents reported in the literature (see comparison chart SI). The relative fluorescence quenching order based on the Stern-Volmer constants derived from PL quenching experiments and upon addition of 120 equivalents (for example) of various electron deficient aromatics was found to be: PA>DNP>Q>PNP>DNT>PNT>NB in 2 as well as 4 (cf. SI). Within a class, it appears that the quenching efficiency increases with the number of nitro groups. It may be readily noticeable that PA has greater quenching efficiency when compared to other NAs; it is ca. 4.5 times higher when compared to that of nitrobenzene. We also found that these larger fluorophores (2

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and 4) are selective to nitrophenols when compared to nitrotoluenes; that is, DNP is 3.5 times effective in quenching the fluorescence when compared to DNT. The  $k_{\alpha}$  values derived from the Stern-Volmer equation ( $\tau$  (2/4) = 2.57 ns,  $\tau$  (5) = 2.72 ns) for 2, 4 and 5 in case of PA, are found to be  $3.73 \times 10^{12}$  M<sup>-1</sup>s<sup>-</sup>  $^{1}$ , 4.63 × 10<sup>12</sup> M<sup>-1</sup>s<sup>-1</sup> and 4.66 × 10<sup>12</sup> M<sup>-1</sup>s<sup>-1</sup>, respectively. These values are two order of magnitude higher than those of the typical diffusion-controlled quenching process (ca. 10<sup>10</sup> M<sup>-1</sup>s<sup>-1</sup>), and hence we attribute this quenching to a static quenching process.<sup>[8,9,43]</sup> We believe that such high values of  $k_{a}$  resulting in a static mechanism, is originated from the introduction of larger  $\pi$ -system for extended electron (or exciton) delocalization. To confirm this static behaviour, we varied the quencher concentration in the fluorophore solution (both 2 and 4) and measured the corresponding fluorescence lifetimes. A straight line with no variation in lifetime ( $\tau_0/\tau = 1$ ) was observed, confirming that it follows a typical static guenching mechanism (Figure 4b).<sup>[43]</sup> This conveys probably a complex (donor-acceptor type) formation between the electron poor PA and the electron rich fluorophores in the ground-state. The absorption spectrum recorded for the fluorophores with varying concentration of the quencher (PA) clearly indicated a tailing effect without change in the absorption spectrum supporting the formation of a nonfluorescent ground-state complex (SI).[42c,43a] A slight increment in  $k_{\alpha}$  values in the cases of **4** and **5** supports enhanced ground state interaction for complex formation possibly through its more contact area (3D). Additionally, fluorescence titrations of 2 and 4 with addition of varying amounts of PA at various excitation wavelengths (320, 342, 360 and 385 nm) were conducted to check the masking effect ("inner-filter effect") of PA (as PA and 2/4 have absorption in the same range of the absorption spectrum). Though the emission intensities observed at various excitation wavelengths were different, their emission profile and



**Figure 4.** a) Changes in fluorescence emission intensity of **2** upon addition of varying amounts of PA. Inset photographs (top) show the fluorescence observed at the initial (0  $\mu$ L, under room light and UV light illumination) and final (500  $\mu$ L) stages of the titration with PA (under UV light illumination). b) Stern-Volmer plot from the changes in fluorescence intensity (black dots) and the changes in lifetime (blue dots) during the titration of PA with **2**.

percentage quenching was found to remain unaltered. Based on this result, we rule out the possibility of fluorescence quenching due to masking by PA.<sup>[42c,43b]</sup>

To further obtain insights into the quenching mechanism, the LUMO level and absorption spectrum of the quencher were compared with the LUMO level and emission spectrum of the fluorophore, respectively. From the electrochemical data, it is clear that the LUMO values of the  $\pi$ -expanded fluorene fluorophores **2** (-2.65 eV), **4** (-2.65 eV) and **5** (-2.66 eV) are now

stabilized due to  $\pi$ -electron delocalization and are very well positioned with the LUMO values of DNT (-3.39 eV), PA (-4.31 eV), etc. for an efficient photo-induced electron transfer (PET) to occur from the electron-rich fluorescent sensor to electrondeficient NACs (Figure 3b). The thermodynamic driving force for this process is calculated to be ca. -1.66 eV and -0.74 eV for PA and DNT, respectively. The observed exergonicity ( $\Delta G_{PET}$  = negative) in the above process, in combination with the high quenching rate constants ( $k_a$ ) support the existence of PET mechanism. Moreover, this corroboration is further confirmed by non-overlapping emission spectrum of the fluorophore and the absorption spectrum of PA (see, SI). Thus, PL quenching with various nitrophenols/nitrotoluenes observed here could be attributed to the donor-acceptor-type charge transfer interaction between the electron rich fluorene and the electron deficient nitroaromatics and not due to the energy transfer mechanism. <sup>1</sup>H NMR spectrum of a mixture of 4 and PA (1:50 equiv., respectively) in CDCl<sub>3</sub> displayed a slight upfield shift for the protons of PA and 4, consistent with the  $\pi$ - $\pi$  interaction, attesting to a typical charge-transfer interaction (SI).

Another important criterion for sensing of analytes is the limit of detection (LOD). The detection limit of these fluorophores (2 and 4) for sensing PA is calculated by plotting the change in fluorescence intensity against [PA]. By curve fitting procedure, LOD can be obtained using the formula: 3 x SD/m; where SD stands for standard deviation and m for the slope value of the calibration curve.<sup>[43a]</sup> LOD calculated for compounds 2 and 4 is 3.8 ppm, and for 5 is 1.8 ppm. The above set of sensing experiments suggests better sensitivity/performance for a spirofluorophore (5, 3D) when compared to the planar derivative 2 (2D), probably because of its possibility to offer large-area (3D) multi-modal interactions (via  $\pi$ - $\pi$ ) with the electron poor aromatics. Fluorescence titrations of the fluorophores 2 and 4 with picric acid (of several dilutions, 10<sup>-2</sup> to 10<sup>-8</sup> M) also clearly suggests that these  $\pi$ -expanded fluorophores have the ability to detect as low concentration of PA as 0.2 ppb or 0.2 ng/mL, which is in comparison to the triptycene-based nanographene sensors.<sup>[11]</sup> It is interesting to notice a marginal preference shown by 3D skeletons in the sensing of nitroaromatics in solution, within this unique set of  $\pi$ -expanded fluorenes.

Visual sensing of nitroaromatic explosive vapors using a solidmatrix is so important that it can have immediate application in military/defence.[44] As these fluorophores 1-5 show excellent PL in ps films, sensing properties (NAs) in solution, we investigated the vapour phase detection of NAs by monitoring the fluorescence quenching behaviour in films of approximately same thickness. The spin-coated ps films of compounds 2 (average film thickness ca. 1.60 µm), 4 (average film thickness ca. 1.56 µm) and 5 (average film thickness ca. 1.58 µm) were exposed to the saturated vapours of PNT (due to its high vapour pressure at room temperature, 4.89 × 10<sup>-2</sup> Torr at 25 °C)<sup>[40b]</sup> for 5 min. The films of the fluorophores 2, 4 and 5 experienced quenching of fluorescence by PNT vapours to a greater extent (up to 87% in 2, 90% in 4 and 94% in 5, respectively, Figure 5a) when compared to that in solution, where contribution of solvent effects and interactions are pivotal. We evaluated the quenching performance of the films of 2 by varying the film thickness. A thinner film of 2 (ca. 1.40 µm) exhibited fluorescence quenching up to 98%, while its thicker film (ca. 3.0 µm) exhibited fluorescence quenching up to 64%. A similar trend was

observed for the films of 4 and 5 as well. These results definitely point to a direct correlation between performance variation and film thicknesses. It has been known from several reports that thinner the film, better the sensitivity is, which is in line with our observation.<sup>[29a,45]</sup> To our excitement, when these quenched films were exposed to saturated hexane vapours for a period of 5 min, the fluorescence was regenerated effectively (84% recovery in case of 2, 67% recovery in case of 4, and 64% recovery in case of 5). The lower recovery observed in the cases of films of fluorenes 4 and 5, when compared to 2, may possibly be attributed to the differences in their molecular structure (or shape, 2D vs 3D) and in their abilities for multi-modal interaction. Indeed, a larger contact area (3D spiro-type, orthogonal πexpanded planes in 4 and 5) that provides better platform for multiple donor-acceptor interactions for binding could probably be the reason for the slow recovery observed for the films of 4 and 5. The above method of regeneration of fluorescence (visible to naked-eye) by exposing the film to solvent vapours, instead of dipping in a solvent, is beneficial as it prevents contamination of solvents via dipping process. To see, if the fluorescence regeneration can be quantitative, the films (2/4/5) after exposing to PNT vapours (quenched) were dipped into hexane, and the fluorescence was regenerated very efficiently (ca. 99%). Thus, nitroaromatics can be detected reversibly using these films, in multiple cycles, which is one of the prime criteria for recyclability.



**Figure 5.** a) Fluorescence spectrum recorded for ps film of **2** before (blue line) and after (red line) exposure to PNT vapours (for 5 min). Inset photographs show blue emission of ps films of **2** and its PL quenching upon exposure to PNT vapors (5 min) under UV-light illumination. Regeneration of fluorescence is noticed upon exposing the films to hexane vapours (5 min). b) Complete PL quenching of the bright blue circle (left, obtained from **2**) on TLC plate by dipcotating PA solution (right). c) Complete PL quenching of the scripts (IITM) written with solution **2** (top) on TLC plate by overwriting with dinitrotoluene DNT solution (bottom, left).

The detection of nitroaromatics were also tested on a solidsupport, such as, silica-gel TLC plate. Initially, the fluorophore was adsorbed on the silica-gel surface of TLC plate by dippainting the fluorophore solution using a paint-brush (photographs, Figures 5b,c). When the quencher solution (DNT/PA) was repainted/dip-coated over the fluorophore traces on TLC, the fluorescence was quenched fully very immediately. This quenching of fluorescence can be immediately detectable by the naked eye under UV-light ( $\lambda_{exc} = 365$  nm) illumination. The fluorescence quenching mechanism in films/solid-supports of **2/4/5** may be viewed as an adsorption of NACs on the surface of the solid matrix via facile donor-acceptor interactions.

In summary, we have successfully demonstrated a strategy for expansion of the  $\pi\mbox{-system}$  of fluorenes via DDQ-mediated

oxidative cyclization, without the need for blocking groups. Through  $\pi$ -expansion, we have improved the absorption characteristics ( $\varepsilon$ ) by shifting the absorption maximum close to the visible region. Importantly, the  $\pi$ -expansion of fluorene moves the emission into the blue region, but does not affect the PLQEs in solution (near unity); PLQE of polystyrene films of spirocompound 5 reached ca. 0.90, which is the highest for any compound in fluorene/spirobifluorene series. The rigidity, coplanarity/spiro-linkage and the larger π-system in 1-5 lead to reduction in bandgap, deepened HOMOs, and high thermal stabilities (up to 540 °C). The synthesized compounds reported herein constitute a new set of  $\pi$ -expanded fluorenes, in that, to our excitement, 3D skeletons reveal a slightly better performance in the sensing behavior, and detect nitroaromatic compounds (PA) at a ppb level. Besides understanding the regioselectivity in fluorenes, we are presently exploring the potential of these bigger and brighter fluorenes in organic electronics, due to their suitable and advantageous characteristics when compared to their high molecular weight oligofluorene/spirobifluorene counterparts. The π-enlarged fluorene/spirobifluorene skeletons reported here may find potential application in sensory devices for homeland security, military operations, etc. due to their high sensitivity and ease of synthesis.

#### **Experimental Section**

The detailed procedure for the synthesis of 2D fluorenes (1-3), 3D spirobifluorenes (4 and 5), their intermediates (1k-4k and 1p-4p) and their complete characterization details, and other photophysical, thermal and electrochemical characterization and single crystal X-ray diffraction details were provided in the supplementary information. Single crystal X-ray diffraction structure of compound 3 can be obtained from CCDC, No: 1505272.

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**Keywords**: π-Expansion • Fluorenes • Photoluminescence • Nitroaromatics • Sensing

- a) Organic Light Emitting Devices. Synthesis, Properties and Applications (Eds.: K. Müllen and U. Scherf), Wiley-VCH: Weinheim, 2006; b) C. Zhang, P. Chen, W. Hu, Small 2016, 12, 1252; c) S. B. Meier, D. Tordera, A. Pertegás, C.-R. Carmona, E. Ortí, H. J. Bolink, Mater. Today 2014, 17, 217; d) I. D. W. Samuel, G. A. Turnbull, Chem. Rev. 2007, 107, 1272; e) S. W. Thomas Iii, G. D. Joly, T. M. Swager, Chem. Rev. 2007, 107, 1339; f) J.-L. Li, H.-C. Bao, X.-L. Hou, L. Sun, X.-G. Wang, M. Gu, Angew. Chem. Int. Ed. 2012, 52, 1830.
- [2] M. Shimizu, T. Hiyama, *Chem. Asian J.* **2010**, *5*, 1516.
- [3] R. Dabestani, I. N. Ivanov, Photochem. Photobiol. 1999, 70, 10.

- [4] a) Y. Y. Long, H. B. Chen, Y. Yang, H. M. Wang, Y. F. Yang, N. Li, K. A. Li, J. Pei, F. Liu, *Macromolecules* 2009, *42*, 6501; b) H. H. Nguyen, X. Li, N. Wang, Z. Y. Wang, J. Ma, W. J. Bock, D. Ma, *Macromolecules* 2009, *42*, 921; c) S. W. Thomas, J. P. Amara, R. E. Bjork, T. M. Swager, *Chem. Commun.* 2005, 4572; d) P. Marks, S. Cohen, M. Levine, *J. Polym. Sci., Part A: Polym. Chem.* 2013, *51*, 4150.
- [5] For small molecule-based approaches via self-assembly, see: (a) K. K. Kartha, A. Sandeep, V. C. Nair, M. Takeuchi, A. Ajayaghosh, *Phys. Chem. Chem. Phys.* 2014, *16*, 18896; (b) T. Naddo, Y. Che, W. Zhang, K. Balakrishnan, X. Yang, M. Yen, J. Zhao, J. S. Moore, L. Zang, *J. Am. Chem. Soc.* 2007, *129*, 6978; (c) K. K. Kartha, S. S. Babu, S. Srinivasan, A. Ajayaghosh, *J. Am. Chem. Soc.* 2012, *134*, 4834; (d) A. Sandeep, V. K. Praveen, K. K. Kartha, V. Karunakaran, A. Ajayaghosh, *Chem. Sci.* 2016, *7*, 4460; (e) K. K. Kartha, A. Sandeep, V. K. Praveen, A. Ajayaghosh, *Chem. Rec.* 2015, *15*, 252; (f) N. Dey, S. K. Samanta, S. Bhattacharya, *ACS Appl. Mater. Interfaces*, 2013, *5*, 8394.
- a) J. V. Goodpaster, V. L. McGuffin, Anal. Chem. 2001, 73, 2004; b) K.
   S. Focsaneanu, J. C. Scaiano, Photochem. Photobiol. Sci. 2005, 4, 817; c) P. Singla, P. Kaur, K. Singh, Tetrahedron Lett. 2015, 56, 2311.
- a) H. Wang, X. Xu, A. Kojtari, H. F. Ji, *J. Phys. Chem. C* 2011, *115*, 20091; b) Y. Z. Liao, V. Strong, Y. Wang, X. G. Li, X. Wang, R. B. Kaner, *Adv. Funct. Mater.* 2012, *22*, 726; c) X. G. Li, Y. Liao, M. R. Huang, V. Strong, R. B. Kaner, *Chem. Sci.* 2013, *4*, 1970.
- [8] P. Sam-ang, D. Raksasorn, M. Sukwattanasinitt, P. Rashatasakhon, RSC Adv. 2014, 4, 58077.
- [9] N. Venkatramaiah, S. Kumar, S. Patil, Chem. Commun. 2012, 48, 5007.
- a) G. V. Zyryanov, M. A. Palacios, P. Anzenbacher, *Org. Lett.* 2008, *10*, 3681; b) P. Anzenbacher, L. Mosca, M. A. Palacios, G. V. Zyryanov, P. Koutnik, *Chem. Eur. J.* 2012, *18*, 12712.
- [11] P.-C. Zhu, L.-N. Luo, P.-Q. Cen, J.-T. Li, C. Zhang, Tetrahedron Lett. 2014, 55, 6277.
- [12] For example: a) S. H. Lee, T. Nakamura, T. Tsutsui, *Org. Lett.* 2001, 3, 2005; b) S. Beaupre, P. L. Boudreault, M. Leclerec, *Adv. Mater.* 2010, 22, E6.
- [13] Annulation at the 3,4 and 5,6-faces of fluorene leading to a helicene has been reported very recently, see: a) O. Hiromi, A. Midori, N. Koji, N. Masanobu, N. Kazuyuki, N. Kyoko, Org. Lett. 2016, 18, 3654; b) H. Oyama, K. Nakano, T. Harada, R. Kuroda, M. Naito, K. Nobusawa, K. Nozaki, Org. Lett. 2013, 15, 2104; For helical bitriphenylenes: c) Y. Sawada, S. Furumi, A. Takai, M. Takeuchi, K. Noguchi, K. Tanaka, J. Am. Chem. Soc. 2012, 134, 4080.
- [14] J. Wu, W. Pisula, K. Mullen, Chem. Rev. 2007, 107, 718.
- [15] J. Wu, M. D. Watson, N. Tchebotareva, Z. Wang, K. Müllen, J. Org. Chem. 2004, 69, 8194.
- [16] D. Xia, T. Marszalek, M. Li, X. Guo, M. Baumgarten, W. Pisula, K. Müllen, Org. Lett. 2015, 17, 3074.
- [17] C.-H. Lee, Y.-Y. Lai, S.-W. Cheng, Y.-J. Cheng, Org. Lett. 2014, 16, 936.
- [18] S. Kumar, D. Karthik, K. R. J. Thomas, M. S. Hundal, *Tetrahedron Lett.* 2014, 55, 1931.
- [19] a) G. Xu, L. Ping, Y. Ma, *Polymer* 2014, *55*, 3083. b) K. T. Wong, Z. J. Wang, Y. Y. Chien, C.-L. Wang, *Org. Lett.* 2001, *3*, 2285; c) F. Moreau, N. Audebrand, C. Poriel, M.-B. Virginie, J. Ouvry, *J. Mater. Chem.*, 2011, *21*, 18715.
- [20] M. Grzybowski, K. Skonieczny, H. Butenschön, D. T. Gryko, Angew. Chem. Int. Ed. 2013, 52, 9900.
- [21] A. A. O. Sarhan, C. Bolm, Chem. Soc. Rev. 2009, 38, 2730.
- [22] For example: a) Y. Zhou, W.-J. Liu, W. Zhang, X.-Y. Cao, Q.-F. Zhou, Y. Ma, J. Pei, *J. Org. Chem.* **2006**, *71*, 6822; b) A. Pradhan, P. Dechambenoit, H. Bock, F. Durola, *Angew. Chem. Int. Ed.* **2011**, *50*, 12582; c) M. Danz, R. Tonner, G. Hilt, *Chem. Commun.* **2012**, 48, 377.
- [23] a) F. Dötz, J. D. Brand, S. Ito, L. Gherghel, K. Müllen, *J. Am. Chem.* Soc. 2000, 122, 7707; b) C. D. Simpson, J. D. Brand, A. J. Berresheim, L. Przybilla, H. J. Rader, K. Müllen, *Chem. Eur. J.* 2002, *8*, 1424; c) X.-G. Li, Y.-W. Liu, M.-R. Huang, S. Peng, L.-Z. Gong, M. G. Moloney, *Chem. Eur. J.* 2010, *16*, 4803; d) X.-G. Li, Y. Liao, M.-R. Huang, R. B.

Kaner, *Chem. Sci.* **2015**, *6*, 7190; e) X.-G. Li, Y. Liao, M.-R. Huang, R. B. Kaner, *Chem. Sci.* **2015**, *6*, 2087.

- [24] B. T. King, J. Kroulík, C. R. Robertson, P. Rempala, C. L. Hilton, J. D. Korinek, L. M. Gortari, J. Org. Chem. 2007, 72, 2279.
- [25] M. L. Tang, Z. Bao, Chem. Mater. 2011, 23, 446.
- [26] a) L. Zhai, R. Shukla, R. Rathore, *Org. Lett.*, **2009**, *11*, 3474; b) L. Zhai,
   R. Shukla, S. H. Wadumethrige, R. Rathore, *J. Org. Chem.* **2010**, *75*, 4748.
- [27] J. B. Birks, Photophysics of Aromatic Molecules; Wiley: New York, 1970.
- [28] A. Bree, R. Zwarich, J. Chem. Phys. 1969, 51, 903.
- [29] a) G. B. Demirel, B. Daglarac, M. Bayindir, *Chem. Commun.* 2013, *49*, 6140; b) P. Beyazkilic, A. Yildirim, M. Bayindir, *ACS Appl. Mater. Interfaces.* 2014, *6*, 4997; c) Y. Wang, A. La, Y. Ding, Y. Liu, Y. Lei, *Adv. Funct. Mater.* 2012, *22*, 3547.
- [30] W. H. Melhuish, J. Phys. Chem. 1961, 65, 229.
- [31] a) T. Serevičius, R. Komskis, P. Adomènas, O. Adoméniené, V. Jankauskas, A. Gruodis, K. Kazlauskas, S. Juršénas, *Phys. Chem. Chem. Phys.* **2014**, *16*, 7089; b) M. P. Aldred, C. Li, G.-F. Zhang, W.-L. Gong, A. D. Q. Li, Y. Dai, D. Ma, M.-Q. Zhu, *J. Mater. Chem.* **2012**, *22*, 7515.
- [32] J. Luo, Y. Zhou, Q.-Z. Niu, Q.-F. Zhou, Y. Ma, J. Pei, J. Am. Chem. Soc 2007, 129, 11314.
- [33] For example: a) X. H. Zhang, M. W. Liu, O. Y. Wong, C. S. Lee, H. L. Kwong, S. T. Lee, K. S. Wu, *Chem. Phys. Lett.* **2003**, *369*, 478; b) O. K. Cheon, J. Shinar, *Appl. Phys. Lett.* **2002**, *81*, 1738.
- [34] T. P. I. Saragi, T. Spehr, A. Siebert, T. Fuhrmann-Lieker, J. Salbeck, Chem. Rev. 2007, 107, 1011.
- [35] W. R. Dawson, W. M. Windsor, J. Phys. Chem. **1968**, 72, 3251.
- [36] For other designs of ours that impede self-quenching, see: a) J. N. Moorthy, P. Venkatakrishnan, P. Natarajan, D. F. Huang, T. J. Chow, J. Am. Chem. Soc. 2008, 130, 17320; b) J. N. Moorthy, P. Venkatakrishnan, P. Natarajan, D. F. Huang, T. J. Chow, Org. Lett., 2007, 9, 5215; c) J. N. Moorthy, P. Venkatakrishnan, P. Natarajan, D. F. Huang, T. J. Chow, Org. Lett., 2007, 9, 5215; c) J. N. Moorthy, P. Venkatakrishnan, P. Natarajan, D. F. Huang, T. J. Chow, Org. Lett., 2007, 9, 5215; c) J. N. Moorthy, P. Venkatakrishnan, P. Natarajan, D. F. Huang, T. J. Chow, Chem. Commun. 2008, 2146; d) J. N. Moorthy, P. Venkatakrishnan, P. Natarajan, Z. Lin, T. J. Chow, J. Org. Chem. 2010, 75, 2599.
- [37] a) M. S. Kwon, Y. Yu, C. Coburn, A. W. Phillips, K. Chung, A. Shanker, J. Jung, G. Kim, K. Pipe, S. R. Forrest, J. H. Youk, J. Gierschner, J. Kim, *Nature Commun.* **2015**, *6*, 8947; b) J. L. Banal, J. M. White, K. P. Ghiggino, W. W. H. Wong, *Scientific Reports* **2014**, *4*, 4635.
- [38] Excited States in Photochemistry of Organic Molecules (Eds.: M. Klessinger, J. Michl), VCH: New York, 1995.
- [39] F. Valiyev, W.-S. Hu, H.-Y. Chen, M.-Y. Kuo, I. Chao, Y. T. Tao, *Chem. Mater.* 2007, 19, 3018.
- [40] a) S. Shanmugaraju, P. S. Mukherjee, Chem. Commun. 2015, 51, 16014; b) X. Sun, Y. Wang, Y. Lei, Chem. Soc. Rev. 2015, 44, 8019.
- [41] V. O. Stern, M. Volmer, *Physik. Zeitschr.* **1919**, *20*, 183.
- [42] a) J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Springer, 3rd edn, 2010; b) D. Zhao, T. M. Swager, *Macromolecules* 2005, *38*, 9377; c) V. Bhalla, A. Gupta, M. Kumar, D. S. Rao, S. K. Prasad, *Appl. Mater. Interfaces* 2013, *5*, 672; d) J. Wang, J. Mei, W. Z. Yuan, P. Liu, A. J. Qin, J. Z. Sun, Y. G. Ma, B. Z. J. Tang, *Mater. Chem.* 2011, *21*, 4056; e) J.-F. Xiong, J.-X. Li, G.-Z. Mo, J.-P. Huo, J.-Y. Liu, X.-Y. Chen, Z.-Y. Wang, J. Org. Chem. 2014, *79*, 11619.
- [43] a) N. Venkatesan, V. Singh, P. Rajakumar, A. K. Mishra, RSC Adv.
  2014, 4, 53484; b) V. Vij, V. Bhalla, M. Kumar, Appl. Mater. Interfaces,
  2013, 5, 5373; c) V. Bhalla, H. Arora, H. Singh, M. Kumar, Dalton Trans.
  2013, 42, 969.
- [44] a) S. Shanmugaraju, S. A. Joshi, P. S. Mukherjee, *J. Mater. Chem.* **2011**, *21*, 9130; For reviews, see: b) R. Miao, J. Peng, Y. Fang, *Mol. Syst. Des. Eng.* DOI: 10.1039/c6me00039h; c) W. Guan, W. Zhou, J. Lu, C. Lu, *Chem. Soc. Rev.* **2015**, *44*, 6981.
- [45] J.-S. Yang, T. M. Swager, J. Am. Chem. Soc. 1998, 120, 11864.







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A bigger glow makes sense: Highly emissive  $\pi$ -expanded fluorenes as well as spirobifluorenes obtained via a regioselective oxidative cyclization procedure were shown to sense nitroaromatics at a ppb level.

Ramakrishna Jagarapu, Venkatakrishnan Parthasarathy\*

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Bigger and Brighter Fluorenes: Facile  $\pi$ -Expansion, Brilliant Emission and Sensing of Nitroaromatics