## Oligotriarylamines

# Oligotriarylamines with a Pyrene Core: A Multicenter Strategy for Enhancing Radical Cation and Dication Stability and Tuning Spin Distribution

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Abstract: Monoamine 1, diamines 2–4, triamine 5, and tetraamine 6 have been synthesized by substituting dianisylamino groups at the 1-, 3-, 6-, and/or 8-positions of pyrene. Diamines 2–4 differ in the positions of the amine substituents. No pyrene–pyrene interactions are evident in the single-crystal packing of 3, 4, and 6. With increasing numbers of amine substituents, the first oxidation potential decreases progressively from the mono- to the tetraamine. These compounds show intense charge-transfer (CT) emission in  $CH_2CI_2$  at around 530 nm with quantum yields of 48–68%. Upon stepwise oxidation by electrolysis or chemical oxidation, these compounds were transformed into radical cations  $1^{++}-6^{++}$ and dications  $2^{2+}-6^{2+}$ , which feature strong visible and

Introduction

Radical cations and dications are not only important intermediates in organic transformations, but also appealing molecular materials for a wide range of applications because of their intriguing electronic, optical, and magnetic properties.<sup>[1]</sup> These species normally possess high energies and are guite reactive. However, considerable advances have been made recently in the characterization of radical cations and dications with long lifetimes and they have even been isolated as stable compounds.<sup>[2]</sup> For example, Komatsu and co-workers obtained radical cations and dications of oligothiophenes stabilized by annulation with bicyclo[2.2.2]octene units,<sup>[3]</sup> long-lived radical cations of monocyclic arenes were obtained by Pampaloni and co-workers by oxidation with NbF5,<sup>[4]</sup> the radical cations of poly(p-phenylene) oligomers were prepared and characterized by Rathore and co-workers,<sup>[5]</sup> and Yamago and Jasti and their co-workers were able to isolate and characterize the cycloparaphenylene radical cation and dication.<sup>[6]</sup> Recently, polycyclic aromatic compounds with open-shell diradical ground states have received considerable attention.<sup>[7]</sup>

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near-infrared absorptions. Time-dependent density functional theory studies suggested the presence of localized transitions from the pyrene radical cation and aminium radical cation, intervalence CT, and CT between the pyrene and amine moieties. Spectroscopic studies indicated that these radical cations and dications have good stability. Triamine **5** and tetraamine **6** formed efficient CT complexes with tetracyanoquinodimethane in solution. The results of EPR spectroscopy and density functional theory calculations suggested that the dications  $2^{2+}-4^{2+}$  have a triplet ground state, whereas  $5^{2+}$  and  $6^{2+}$  have a singlet ground state. The dication of 1,3-disubstituted diamine **4** exhibits a strong EPR signal.

Aminium radical cations, obtained by the oxidation of  $\pi$ conjugated arylamine derivatives, have been the subject of intense research activity.<sup>[8]</sup> One of the earliest and most notable examples is Wurter's Blue, the radical-cation form from tetramethyl-p-phenylenediamine.<sup>[9]</sup> By using weakly coordinating anions, Wang and co-workers recently succeeded in isolating benzidine and aniline radical cations,<sup>[10]</sup> among other organic radical cations.<sup>[11]</sup> Kamada, Yamamoto, and co-workers demonstrated that bis(acridine) dimers with diradical character show much larger two-photon absorption cross-sections than closed-shell compounds with the same structural backbone and composition.<sup>[12]</sup> Monoradical cations of bis(triarylamine) compounds have been investigated as mixed-valence (MV) systems to probe basic electron-transfer processes.<sup>[13]</sup> Bis(triarylamine) compounds with strong charge delocalization possess intense near-infrared (NIR) absorptions in the MV state, and polymeric films based on these materials show interesting NIR electrochromism.<sup>[14]</sup> In addition, compounds containing multiple aminium radical cations are promising high-spin organic materials.<sup>[15]</sup> In all of these studies, the stability of the aminium radical cations and/or dications is crucial for their physical properties and optoelectronic performance.

Pyrene and pyrene derivatives are some of the most used fluorescent probes and organic semiconductors.<sup>[16]</sup> Electrophilic substitution at the 1-, 3-, 6-, and/or 8-positions of pyrene and subsequent transformation have led to enormous organic molecules that have been used in electric and optoelectronic devices.<sup>[16]</sup> The pyrene radical cation (Pyr<sup>\*+</sup>) is normally highly reactive and its characterization is difficult. Dietrich and Heinze

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were able to observe reversible two-step oxidative waves for pyrene by cyclic voltammetry (CV) in liquid SO<sub>2</sub> at low temperature,<sup>[17]</sup> however, the oxidation of pyrene is usually irreversible at room temperature in conventional solvent. Pyrene derivatives bearing peripheral dimethylaminoethynyl units show enhanced radical stability and electrogenerated chemiluminescence,<sup>[18]</sup> however, the electrochemical oxidation is still irreversible in the timescale of CV. Interestingly, Rathore and co-workers successfully isolated the radical cation of tetraisopropylpyrene.<sup>[19]</sup> This compound showed a reversible oxidation wave at + 0.98 V versus SCE and an intense Pyr<sup>++</sup>-associated absorption band at 494 nm. Similar absorption bands (ca. 460 nm) have been observed by Oyama and Matsui for a number of 1-substituted pyrene radical cations by an electron-transfer stoppedflow method.<sup>[20]</sup>

We present herein a combined experimental and theoretical study of six triarylamine derivatives with a pyrene core (1-6), Figure 1). From compound 1 to 2-4, 5, and 6, the number of di-*p*-anisylamino groups progressively increases from 1 to 4.



Figure 1. Compounds 1–6 studied in this paper.

Compounds 2–4 are diamine derivatives with two di-*p*-anisylamino groups at different positions of the pyrene core. We expected that, by attaching multiple redox-active amino groups to the pyrene core, the stability of the corresponding radical cations and dications would be significantly enhanced. Compounds 1–6 have been studied by single-crystal X-ray crystallographic, electrochemical, and spectroscopic analysis. In addition, the radical cations and dications of these compounds have been studied by electronic absorption and electron paramagnetic resonance (EPR) spectroscopy. Finally, density functional theory (DFT) and time-dependent DFT (TDDFT) computations were carried out to elucidate the spin distributions and absorption assignments.

## **Results and Discussion**

#### Synthesis and single-crystal X-ray structures

Mono- and diamine compounds **1–4** were synthesized from the palladium-catalyzed C–N coupling reactions between di-*p*anisylamine and the corresponding pyrene bromides, 1-bromopyrene, 1,8-dibromopyrene,<sup>[21]</sup> 1,6-dibromopyrene, and 1,3-dibromo-7-*tert*-butylpyrene,<sup>[22]</sup> respectively (see details in the Experimental Section). Triamine **5** and tetraamine **6** were isolated from the reaction of di-*p*-anisylamine with 1,3,6,8-tetrabromopyrene.<sup>[23]</sup> The isolation of **5** was unexpected but reasonable, as a result of the replacement of one bromine atom by a hydrogen atom during the palladium-catalyzed transformation. These compounds have been fully characterized. In addition, single-crystal X-ray structures for **3**, **4**, and **6** were determined (Figure 2 and Table S1 in the Supporting Information). In these



**Figure 2.** Single-crystal X-ray structures of (a) **3**, (b) **4**, (c) top view of **6**, and (d) side view of **6**. Ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

compounds, the nitrogen atoms are bonded to three aryl groups to form three-wheel propeller structures. No pyrenepyrene interactions are evident in the crystal packing of these compounds (see Figures S1, S3, and S4) owing to the steric hindrance of the anisyl groups.

Compounds **4** and **6** show interesting lamellar crystal packing (Figures 3 and 4). The pyrene core of **4** stands upright from the side view of the lamellar structures. In each layer, the *tert*butyl groups of neighboring molecules are alternately directed up and down. In the lamellar packing of **6**, the pyrene core lies in the plane of each layer and the eight anisyl groups of each molecule keep each layer well separated from each other.

#### **Electrochemical studies**

Figure 5 shows the CVs and differential pulse voltammograms (DPVs) of **1–6** in CH<sub>2</sub>Cl<sub>2</sub>. Monoamine **1** shows a chemically reversible redox wave at  $\pm 0.72$  V versus Ag/AgCl. Diamines **2–4** display two well-separated redox couples in a similar potential window. The first redox wave of **2–4** is at  $\pm 0.61$  to  $\pm 0.63$  V (Table 1). Triamine **5** shows three waves at  $\pm 0.51$ ,  $\pm 0.60$ , and  $\pm 1.18$  V, respectively. When the conventional electrolyte,  $nBu_4$ NClO<sub>4</sub>, was used during the measurement of tetraamine **6**, two two-electron processes at  $\pm 0.44$  and  $\pm 1.21$  V were observed. However, the first wave split into two when  $nBu_4$ NB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> with weakly coordinating anions was used.<sup>[24]</sup> These waves are associated with the oxidation of both amine (N<sup>0/++</sup>) and pyrene moieties (Pyr<sup>0/+</sup>), which will be further discussed later. At more positive potentials, some chemically irreversible events can be observed (see Figure S2 in the Support-



**Figure 3.** (a) Lamellar crystal packing of **4** viewed along the *b* axis. (b) Top view of the middle layer in (a).

ing Information). These are associated with the irreversible oxidation of the in situ generated aminium cation radicals<sup>[25]</sup> or the pyrene core. The radical cations of **2–4** and dications of **5** and **6** have large comproportionation constants,  $K_c$  (Table 1), which suggests that they have good thermodynamic stability.

The above electrochemical results show that the first oxidation potentials of **1–6** progressively shift to the less positive region as more amine substituents are attached to the pyrene



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**Figure 4.** (a) Lamellar crystal packing of **6** viewed along the a axis. (b) Top view of each layer.

core. This suggests that the stability of the resulting radical cations can be efficiently enhanced by increasing the number of amine substituents. Note that pristine pyrene exhibits an irreversible oxidation at potentials more positive than +1.3 V versus Ag/AgCl (see Figure S3 in the Supporting Information). On the basis of the electrochemical data, the highest-occupied molecular orbitals (HOMOs) were estimated to be -5.4 eV for 1, -5.3 eV for 2–4, -5.2 eV for 5, and -5.1 eV for 6 in a vacuum. This means that the HOMOs of these compounds are progressively destabilized with increasing amine substituents. This trend correlates with the results of the DFT calculations; the HOMOs of 1–6 were calculated to be -5.99, -5.85, -5.90, -5.77, and -5.70 eV, respectively (Figure 6). It is

interesting to note that the lowest-unoccupied molecular orbitals (LUMOs) of 1-6 are all dominated by the pyrene moiety; however, the orbital compositions of the HOMOs differ significantly. The HOMO of 1 is dominated by the triarylamine component whereas the HOMOs of the diamines 2-4 are localized across the whole molecule. In contrast, the pyrene frameworks of 5 and 6 make a more important contribution to their HOMOs.

Table 1. Electrochemical, absorption, and emission data in CH2Cl2.									
Comp.	E <sub>1/2</sub> [V]	$\Delta E_{(1,2)} / \Delta E_{(2,3)}$ [mV] <sup>[b]</sup>	$K_{C(1,2)}/K_{C(2,3)}^{[c]}$	E <sub>anodic</sub> <sup>[d]</sup> [V]	$\lambda_{abs,max}$ [nm]	λ <sub>emi,max</sub> [nm]	$\Phi^{ ext{[e]}}$ [%]	τ [ns]	
1	+0.72	_/_	_/_	+ 1.35	416	529	48	12	
2	+0.61, +0.79	180/-	1120/-	+1.46	442	530	52	11	
3	+0.62, +0.80	180/-	1120/-	+1.47	445	531	58	10	
4	+0.63, +0.96	330/-	3.9×10⁵/-	+1.36	434	523	66	10	
5	+0.51, +0.60, +1.18	90/580	33/6.8×10 <sup>9</sup>	+1.55	465	529	48	9	
6	+0.44 (2e), +1.21 (2e)	-/770	$-/1.1 \times 10^{13}$	+1.54	487	525	68	8	
<b>6</b> <sup>[f]</sup>	+0.31, +0.39, +1.30 (2e)	80/910	23/2.6×10 <sup>15</sup>	+ 1.92	-	-	-	-	
[a] Potentials are reported versus $A\alpha/A\alpha(1, nRu, NCIO)$ , was used as the electrolyte unless otherwise noted									

[a] Potentials are reported versus Ag/AgCl.  $nBu_4NClO_4$  was used as the electrolyte unless otherwise noted. [b]  $\Delta E_{(1,2)}$  and  $\Delta E_{(2,3)}$  represent the potential difference between the mono- and dioxidized forms and the diand trioxidized forms, respectively. [c] The comproportionation constant  $K_c$  was determined from  $K_c = 10^{(\Delta E/59)}$ by using  $\Delta E_{(1,2)}$  and  $\Delta E_{(2,3)}$ . [d] Anodic peak potential for an irreversible oxidation. [e] The emission quantum yield was determined by using quinine sulfate as reference with an error of  $\pm 5\%$ . [f]  $nBu_4NB(C_6F_5)_4$  was used as the electrolyte.

Chem. Eur. J. 2014, 20, 17454-17465





others were recorded with nBu<sub>4</sub>NClO<sub>4</sub> as electrolyte.

*E* / V vs Ag/AgCl *E* / V vs Ag/AgCl Figure 5. (a) CVs and (b) DPVs of 1–6 in CH<sub>2</sub>Cl<sub>2</sub> at 100 mV s<sup>-1</sup>. The bottom CV and DPV curves of 6 were recorded with  $nBu_4NB(C_6F_5)_4$  as electrolyte, the Eigure 5. (b) CV s Ag/AgCl



Figure 7. (a) Absorption and (b) emission spectra of 1-6 in CH<sub>2</sub>Cl<sub>2</sub>.



Figure 6. DFT-calculated energy diagrams (left) and isodensity plots of the LUMOs and HOMOs of 1-6.

#### Spectroscopic studies

The electronic absorption and emission spectra of compounds 1-6 in dilute solutions are shown in Figure 7 and the corresponding data are summarized in Table 1. The absorption bands between 350 and 550 nm have been attributed to intramolecular charge-transfer (ICT) transitions from the amine moieties to the pyrene core. This is supported by the results of a TDDFT analysis of 1 (see Figure S4 in the Supporting Information). The predicted S<sub>1</sub> (S=singlet) excitation of HOMO $\rightarrow$ (LUMO) character is responsible for the observed absorptions in the range 350–550 nm. The ICT absorption maxima for 1-6 are 416, 442, 445, 434, 465, and 487 nm, respectively, in CH<sub>2</sub>Cl<sub>2</sub>. Those of the tri- and tetraamines are distinctly bathochromically shifted relative to the others. The data are consistent with the results of the DFT analysis, and indicate that the HOMO-LUMO energy gaps for 1-6 are 5.47, 5.26, 5.27, 5.34, 5.13, and 5.00 eV, respectively. Thus, the frontier MO energy gap becomes increasingly narrow with increasing numbers of amine substituents. The ICT absorptions of **1–6** show bathochromic shifts of 3–6 nm in toluene and hypsochromic shifts of 2–6 nm in  $CH_3CN$  relative to those in  $CH_2Cl_2$  (see Figure S5 and Table S2).

All the compounds are highly emissive in CH<sub>2</sub>Cl<sub>2</sub> solutions ( $\lambda_{max,emi} \approx 530$  nm) with quantum yields of 48–68% and excitedstate lifetimes of around 10 ns. The emissions have been attributed to polarized ICT, as supported by the significant hypsochromic shifts observed in nonpolar solvents (ca. 30 nm shift, see Figure S6 and Table S2 in the Supporting Information).<sup>[26]</sup> No excimer emission was observed for any of the compounds at a high concentration of  $1 \times 10^{-4}$  M. This again indicates that possible pyrene–pyrene interactions are inhibited in these compounds, making them appealing for use in light-emitting devices.<sup>[27]</sup>

To characterize the spectroscopic properties of their radical cations and dications, 1-6 were subjected to stepwise oxidations with SbCl<sub>5</sub> in CH<sub>2</sub>Cl<sub>2</sub>. The absorption spectral changes are shown in Figures 8–10 and the absorption maxima and molar



absorptivities of 1-6 bearing different charges are summarized in Table 2.

When **1** was subjected to one-electron oxidation, the ICT bands decreased significantly and strong visible/NIR absorptions appeared (Figure 8). Absorption bands in the region 500–600 nm with well-defined substructures are very likely from Pyr<sup>++</sup>.<sup>[19,20]</sup> The intense absorption at 760 nm has been attributed to the aminium radical cation  $(N^{++})^{[13-15]}$  and the absorption at 1122 nm has been assigned to the ICT transition from pyrene to  $N^{++}$ , which will be further discussed later. The occurrence of  $N^{++}$ -localized and pyrene  $\rightarrow N^{++}$  ICT transitions suggests that the radical spin is dominated by the triarylamine unit. However, the appearance of Pyr<sup>++</sup> absorptions suggests that the pyrene framework was also partially oxidized.

Figure 9 shows the absorption spectral changes of the three diamine compounds upon the first (mono-oxidation) and second (dioxidation) one-electron oxidations with SbCl<sub>5</sub>. The radical cations  $2^{+}$  and  $3^{+}$  display similar NIR absorptions at around 2000 nm. These bands possibly have intervalence CT (IVCT) and amine $\rightarrow$ Pyr<sup>+</sup> CT character. The dications  $2^{2+}$  and



Figure 8. Absorption spectral changes of 1 upon one-electron oxidation with 1 equiv  ${\rm SbCl}_5$  in  ${\rm CH}_2{\rm Cl}_2.$ 

Table 2. Absorption data of 1-6 with different charges obtained by oxidation with  $\text{SbCl}_{\text{s}}$  in  $\text{CH}_2\text{Cl}_2.$ 

	$\lambda_{\rm abs,max}$ [nm] ( $\epsilon$ [10 <sup>5</sup> ${ m M}^{-1}$ cm <sup>-1</sup> ])
1	388 (0.12), 416 (0.13)
1*+	502 (0.066), 541 (0.12), 590 (0.19), 760 (0.21), 1122 (0.15)
2	442 (0.17)
<b>2'</b> +	628 (0.18), 678 (0.23), 864 (0.032), 1960 (0.12)
<b>2</b> <sup>2+</sup>	628 (0.13), 1048 (0.35)
3	403 (0.16), 445 (0.25)
<b>3.</b> +	624 (0.25), 678 (0.33), 1940 (0.18)
<b>3</b> <sup>2+</sup>	632 (0.14), 1033 (0.54)
4	383 (0.14), 434 (0.19)
<b>4·</b> +	481 (0.14), 596 (0.29), 739 (0.056), 942 (0.091), 2130 (0.055)
<b>4</b> <sup>2+</sup>	579 (0.18), 790 (0.34), 1134 (0.099), 1750 (0.039)
5	392 (0.15), 465 (0.27)
<b>5</b> <sup>+</sup>	452 (0.17), 640 (0.21), 703 (0.25), 1530 (0.12)
<b>5</b> <sup>2+</sup>	452 (0.18), 963 (0.27)
<b>5</b> <sup>3+</sup>	518 (0.16), 856 (0.38), 1059 (0.39)
6	398 (0.19), 487 (0.39)
<b>6'</b> +	462 (0.24), 667 (0.16), 732 (0.27), 1275 (0.11)
<b>6</b> <sup>2+</sup>	425 (0.25), 850 (0.30)
<b>6</b> <sup>4+</sup>	544 (0.23), 814 (0.75), 1012 (0.27)

 $3^{2+}$  show intense absorption peaks at around 1040 nm, which have been assigned to a mixture of N<sup>\*+</sup>-localized and pyrene $\rightarrow$ N<sup>\*+</sup> ICT transitions (see discussion on TDDFT later). The absorption spectra of the 1,3-disubstituted diamine 4<sup>\*+</sup> and 4<sup>2+</sup> are different to those of the radical cations and dications of diamines 2 and 3. The radical cation 4<sup>\*+</sup> shows rather weak and broad NIR absorptions. In contrast, the dication 4<sup>2+</sup> exhibits three distinct bands at 790, 1134, and 1750 nm. The former two peaks have been assigned to N<sup>\*+</sup>-localized and pyrene $\rightarrow$ N<sup>\*+</sup> ICT transitions, respectively, and appear in the same region as the absorptions of 1<sup>\*+</sup>. The peak at 1750 nm may have similar ICT character.



Figure 9. Absorption spectral changes of (a,b) 2, (c,d) 3, and (e,f) 4 upon (a,c,e) mono- and (b,d,f) dioxidation with SbCl<sub>5</sub> in CH<sub>2</sub>Cl<sub>2</sub>. \*: Artefacts.

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Figure 10. Absorption spectral changes of (a,b,c) 5 and (d,e,f) 6 upon (a,d) mono-, (b,e) di-, (c) tri-, and (d) tetra-oxidation with SbCl<sub>5</sub> in CH<sub>2</sub>Cl<sub>2</sub>. \*: Artefacts.

In comparison with the diamine radical cations, the NIR absorptions of triamine **5**<sup>++</sup> and tetraamine **6**<sup>++</sup> are progressively shifted to higher-energy regions (centered at 1530 and 1275 nm, respectively; Figure 10). As shown in Figure S7 in the Supporting Information, these peaks can be deconvoluted into multiple Gaussian functions and the origin of these peaks should be very complex. The results of the TDDFT analyses suggest that these peaks have a large contribution from amine  $\rightarrow$ Pyr<sup>++</sup> ICT transitions. Similarly, the NIR absorptions of dications **5**<sup>2+</sup> and **6**<sup>2+</sup>, at 963 and 850 nm, respectively, consist of several sub-bands. N<sup>++</sup>-localized transitions become more important in higher redox states (856 nm for **5**<sup>3+</sup> and 814 nm for **6**<sup>4+</sup>). The assignments of these absorptions will be further discussed later.

In addition to chemical oxidation, compounds **1–6** were subjected to stepwise oxidation by electrolysis at an indium tin oxide (ITO) glass electrode in  $CH_2Cl_2$  (see Figures S8 and S9 in the Supporting Information). In general, similar absorption spectral changes are observed by chemical oxidation and electrolysis, and the spectral changes can be reversed by decreasing the applied potential during the spectroelectrochemical measurements. The high redox states of **5** and **6** (**5**<sup>3+</sup> and **6**<sup>4+</sup>) are only accessible by chemical oxidation; the attempt to access **5**<sup>3+</sup> and **6**<sup>4+</sup> by electrolysis failed, possibly because the oxidation potentials needed are too high.

The stabilities of the radical cations and dications were tested by monitoring the absorption spectral changes during spectroelectrochemical measurements. For example, when monoamine 1 ( $1 \times 10^{-4}$  m in CH<sub>2</sub>Cl<sub>2</sub> in the presence of electrolyte) was oxidized to 1<sup>++</sup> by electrolysis, the applied potential was switched off and the solutions were left to stand under ambient conditions. The spectral changes show that around half of the radical cations 1<sup>++</sup>-6<sup>++</sup> turn into neutral 1–6 in 30, 60, 60, 60, 180, and 30 min, respectively. This means that the

di- and triamine radical cations are slightly more stable than the monoamine radical cation. The relatively low stability of the tetraamine radical cation is due to the small value of  $K_c$  for  $6^{+}$ . As for the dications,  $5^{2+}$  and  $6^{2+}$  are slightly more stable than  $2^{2+}-4^{2+}$ . The spectral changes show that around half of the  $2^{2+}-4^{2+}$  dications are transformed into radical cations in 15 min, whereas around 30 min is needed for this conversion for  $5^{2+}$  and  $6^{2+}$ .

Compounds **1–6** exhibit low oxidation potentials and destabilized HOMOs, and therefore they can be considered as good electron donors. The possibility of forming charge-transfer (CT) complexes<sup>[28]</sup> of these compounds with the typical electron acceptor tetracyanoquinodimethane (TCNQ) was examined. Figure 11 shows the absorption spectra of 1:1 mixtures of **1–6** with TCNQ in CH<sub>2</sub>Cl<sub>2</sub> at a concentration of  $1 \times 10^{-2}$  M. It is clear that considerable quantities of CT complexes are formed in the solutions **5** or **6** with TCNQ. The three absorption peaks at 695, 750, and 850 nm are characteristic of TCNQ<sup>--</sup>. For example, similar absorptions at 686, 748, and 850 nm were observed by



Figure 11. Absorption spectra of 1:1 mixtures of 1-6 with TCNQ at  $1 \times 10^{-2}$  M in CH<sub>2</sub>Cl<sub>2</sub>.



Weiss and co-workers for TCNQ<sup>--</sup> in CH<sub>2</sub>Cl<sub>2</sub> following electrolysis of neutral TCNQ.<sup>[29]</sup> The appearance of the absorption band at 1300 nm in the spectrum of the mixture of **6** and TCNQ indicates the formation of **6**<sup>++</sup>. However, the mixture of **5** and TCNQ shows an absorption band at around 1000 nm, which points to the formation of **5**<sup>2+</sup> rather than **5**<sup>++</sup> in this mixture. The reason for this difference is unclear at this stage. The amounts of CT complexes formed in other mixtures are much smaller. In dilute solutions (e.g.,  $c = 1 \times 10^{-4}$  M), none of the compounds showed absorption of TCNQ<sup>--</sup>.

#### **EPR studies**

The radical cations of **1–6** all display a single-line EPR signal at around g=2.0 (Figure 12). In the dication form,  $2^{2+}$  and  $3^{2+}$  show a triple-line signal, however, the signal intensity is much lower than that of their radical cations. In comparison, the EPR signal of the dication  $4^{2+}$  is rather strong. The dications of triamine  $5^{2+}$  and tetraamine  $6^{2+}$  show very weak EPR signals (essentially no signal for  $6^{2+}$ ). These results suggest that  $2^{2+}$ ,  $3^{2+}$ , and  $4^{2+}$  are mainly in the triplet ground state, and that  $5^{2+}$  and  $6^{2+}$  are largely in the singlet state. This will be discussed later with the aid of theoretical calculations.

## DFT and TDDFT calculations on the radical cations and dications

The radical cations  $1^{\cdot+}-6^{\cdot+}$  were subjected to DFT calculations at the UCAM-B3LYP/6-31G\*/CPCM/CH\_2Cl\_ level of theory (see



Figure 12. EPR spectra of  $1^{+}-6^{+}$  and  $2^{2+}-6^{2+}$  at room temperature obtained by oxidation with SbCl<sub>5</sub> in CH<sub>2</sub>Cl<sub>2</sub>.

details in the Experimental Section). The Mulliken spin ( $\alpha$ - $\beta$ ) density population plots are shown in Figure 13. In monoamine 1<sup>•+</sup>, the dianisylamine group and the pyrene core have spin densities of 0.664 and 0.205, respectively. This further indicates that the oxidation of 1 is largely based on the pyrene framework. In the di-, tri-, and tetraamine radical cations, the contribution from the pyrene core increases significantly (0.4– 0.7). In 2<sup>•+</sup> and 3<sup>•+</sup>, the spins are delocalized across the whole molecule, with comparable spin contributions from both the triarylamine and pyrene units. For 4<sup>•+</sup>, 5<sup>•+</sup>, and 6<sup>•+</sup>, the spin is more biased towards the pyrene framework and the spin contribution of each dianisylamino group is less than 0.2. Note that care should be taken in the interpretation of these DFT results as it is well known that DFT calculations overestimate charge delocalization.

The geometries of the dications  $2^{2+}-6^{2+}$  were optimized for both the closed-shell singlet state and the open-shell triplet state. The singlet states of  $2^{2+}-4^{2+}$  were calculated to be 3.62, 3.64, and 10.48 kcal mol<sup>-1</sup> higher in energy than their triplet



**Figure 13.** DFT-calculated Mulliken spin distributions of (a–f)  $1^{+}-6^{+}$  (in the doublet state) and (g–i)  $2^{2+}-4^{2+}$  (in the triplet state) at the UCAM-B3LYP/6-31G\*/CPCM/CH<sub>2</sub>Cl<sub>2</sub> level of theory and a schematic representation of the spin contributions on the pyrene core and each dianisylamino group (NAr<sub>2</sub>).

Chem. Eur. J. 2014, 20, 17454 - 17465



states. In contrast, the singlet states of  $5^{2+}$  and  $6^{2+}$  are 4.22 and 9.31 kcal mol<sup>-1</sup> lower in energy than their triplet states. This is in agreement with the EPR results, which indicated that the ground states of  $2^{2+}-4^{2+}$  are triplet states, and those of  $5^{2+}$  and  $6^{2+}$  are singlet states. The lower panel of Figure 13 shows the spin populations of triplets  $2^{2+}-4^{2+}$ ; in each molecule the spins are dominated by two dianisylamino groups.

Next, TDDFT calculations were performed on the DFT-optimized structures to rationalize the absorptions of these compounds in different redox states. Figure 14 shows the TDDFTpredicted doublet (D) excitations and absorption spectra of 1<sup>.+</sup> . The predicted absorptions agree well with the experimental data, although they are a little higher in energy than in the recorded spectrum. The D<sub>1</sub> excitation at 900 nm is responsible for the observed absorption of 1<sup>•+</sup> at 1122 nm. This excitation is associated with  $\beta$ -spin excitation from the highest-occupied spin orbital (HOSO, localized on the pyrene framework) to the lowest-unoccupied spin orbital (LUSO, localized on the dianisylamino unit), which suggests an ICT transition from pyrene to N<sup>++</sup>. The D<sub>2</sub> excitation at 683 nm of  $\beta$ -HOSO-1 $\rightarrow\beta$ -LUSO character is related to the observed N<sup>++</sup>-localized transition at 760 nm. The D<sub>3</sub> excitation at 566 nm is related to the observed Pyr<sup>•+</sup>-localized transitions at 541 and 590 nm.

The TDDFT-predicted doublet excitations for  $2^{++}$  and triplet (T) excitations for  $2^{2+}$  are shown in Figure 15. The D<sub>1</sub> excitation of  $2^{++}$  at 1516 nm has a large contribution from a  $\beta$ -HOSO (delocalized across the whole molecule) $\rightarrow\beta$ -LUSO (more biased towards the pyrene framework) transition (f=0.327), which is related to the absorption at 1960 nm observed experimentally. This transition is better interpreted as an amine $\rightarrow$ Pyr<sup>++</sup> CT transition. However, the occurrence of an IVCT transition be-



**Figure 14.** TDDFT-predicted low-energy doublet (D) excitations and the spin orbitals of 1<sup>++</sup> involved. The experimentally observed absorption spectrum of 1<sup>+</sup> is included for comparison.



**Figure 15.** (a) TDDFT-predicted low-energy doublet (D) excitations and the spin orbitals of **2'**<sup>+</sup> involved and (b) the predicted low-energy triplet (T) excitations and the spin orbitals of **2**<sup>2+</sup> involved. The absorption spectra of **2'**<sup>+</sup> and **2**<sup>2+</sup> are included for comparison.

tween two amine components is also possible. The observed NIR absorption at 1048 nm for the dication  $2^{2+}$  is mainly associated with  $T_1$  and  $T_3$  excitations. The  $T_1$  excitation at 798 nm has  $\beta$ -HOSO (localized on pyrene) $\rightarrow\beta$ -LUSO (localized on amine) character (f=0.327) and has been attributed to the ICT transition from pyrene to N<sup>++</sup>. The  $T_3$  excitation at 737 nm is of  $\beta$ -HOSO–2 (localized on amine) $\rightarrow\beta$ -LUSO character (f=0.693), indicative of N<sup>++</sup>-localized transitions. The radical cations and dications of **3** have very similar experimental and predicted absorption spectra to those of **2** (see Figures S10 and S11 in the Supporting Information).

The results of TDDFT calculations for **4**<sup>•+</sup> are shown in Figure S12. The predicted D<sub>1</sub> excitation at 1445 nm is of  $\beta$ -HOSO $\rightarrow\beta$ -LUSO character (f=0.141). This can be regarded as an amine $\rightarrow$ Pyr<sup>++</sup> CT transition, which appears as a broad NIR band at 2130 nm in the recorded spectrum (Figure 9e). Fig-

Chem. Eur. J. 2014, 20, 17454-17465



ure S13 shows the TDDFT-predicted triplet excitations of  $4^{2+}$ , which are unable to explain the observed low-energy absorptions at 1134 and 1750 nm. The T<sub>2</sub> and T<sub>3</sub> excitations are mainly related to the N<sup>++</sup>-localized transitions observed at 790 nm.

Figure 16 shows the TDDFT results for **5**<sup>++</sup> and **5**<sup>2+</sup>. The predicted D<sub>1</sub> and D<sub>2</sub> transitions are related to the observed NIR absorptions of **5**<sup>++</sup>. The D<sub>1</sub> transition is of  $\beta$ -HOSO-1 (dominated by the dianisylamino units) $\rightarrow \beta$ -LUSO (dominated by pyrene) character ( $\lambda = 1143$  nm, f = 0.357), and the D<sub>2</sub> transition is of  $\beta$ -HOSO (dominated by the dianisylamino units) $\rightarrow \beta$ -LUSO character ( $\lambda = 1035$  nm, f = 0.141). These transitions have been attributed to amine  $\rightarrow$ Pyr<sup>++</sup> CT excitations. The above EPR and DFT results suggest that dication **5**<sup>2+</sup> has a singlet ground state. Therefore TDDFT calculations were also performed on the closed-shell singlet state of **5**<sup>2+</sup>, which showed that the predicted S<sub>1</sub> and S<sub>2</sub> transitions are related to the observed NIR absorptions of **5**<sup>2+</sup>. Interestingly, the S<sub>1</sub> (HOMO $\rightarrow$ LUMO) and



**Figure 16.** (a) TDDFT-predicted low-energy doublet (D) excitations and the spin orbitals of  $5^+$  involved and (b) the predicted low-energy singlet (S) excitations and the molecular orbitals of  $5^{2+}$  involved. The absorption spectra of  $5^+$  and  $5^{2+}$  are included for comparison.

 $S_2$  (HOMO-1  $\rightarrow$  LUMO) transitions for  $5^{2+}$  exhibit very similar orbital changes with respect to the  $D_2$  and  $D_1$  transitions for  $5^{\cdot+}$  and are also mainly of amine  $\rightarrow$  Pyr\*+ CT character.

The TDDFT results for **6**<sup>++</sup> and **6**<sup>2+</sup> (see Figures S14 and S15 in the Supporting Information) show some similarities to those for **5**<sup>++</sup> and **5**<sup>2+</sup>. The predicted D<sub>1</sub>, D<sub>2</sub>, and D<sub>3</sub> transitions are related to the observed NIR absorptions of **6**<sup>++</sup>, and the predicted S<sub>1</sub>, S<sub>2</sub>, and S<sub>3</sub> transitions are related to the observed NIR absorptions of **6**<sup>2+</sup>. All of these transitions have mainly been attributed to amine  $\rightarrow$ Pyr<sup>++</sup> CT transitions. These results suggest that the mono- and dioxidations of **5** and **6** are dominated by pyrene oxidation with the amino units acting as electron-donating substituents to stabilize the resulting radical cations and dications.

## Conclusion

We have demonstrated in this work that by increasing the number of dianisylamino substituents on the pyrene core, the oxidation potentials of the materials decrease progressively and the stabilities of the corresponding radical cations and dications are enhanced. Such a multicenter strategy provides new guidelines for the design and synthesis of organic optoelectronic materials with multielectron redox capability. The oligotriarylamine derivatives reported in this work are good electron donors, have interesting optoelectronic properties, and have potential uses in many areas. In addition, triamine 5 and tetraamine 6 are able to form efficient CT complexes with TCNQ in solution. These oligotriarylamines have potential use as hole-transporting materials in optoelectronic devices.<sup>[30]</sup> All pyrene-amine adducts (1-6) reported in this work are highly emissive. No pyrene-pyrene interactions are evident in the single-crystal X-ray analyses of 3, 4, and 6, which may make them appealing for use in light-emitting devices.<sup>[27]</sup> The 1,3-dianisylaminopyrene compound shows an intense EPR signal in the dication form and is useful in the preparation of organic spin materials.[15]

The spin distribution and NIR transitions in different redox states can be tuned by varying the number of dianisylamino substituents. All the materials are in the doublet state in the radical-cation form. The monoamine radical cation is better described as an aminium radical cation, the free spin in the diamine radical cations is delocalized across the whole molecule, and the tri- and tetraamine radical cations are better described as pyrene radical cations. In the dication form, the diamine compounds are in the triplet ground state, whereas the triand tetraamine dications are in the singlet ground state, as supported by EPR and DFT analyses.

## **Experimental Section**

**Spectroscopic measurements**: Absorption spectra were recorded by using a Perkin-Elmer Lambda 750 UV/VIS/NIR spectrophotometer at room temperature in the denoted solvents with a conventional 1.0 cm quartz cell. Spectroelectrochemistry was performed in a thin-layer cell (optical length = 0.2 cm) in which an ITO glass electrode (<10  $\Omega$ /square) was set in the indicated solvent containing

Chem. Eur. J. 2014, 20, 17454-17465



A platinum wire and Ag/AgCl in saturated aqueous NaCl solutionwas used as a counter electrode and reference electrode, respectively. The cell was placed in the spectrophotometer to monitor spectral changes during electrolysis.

**Electrochemical measurements:** All CV and DPV measurements were made by using a CHI 620D potentiostat with a one-compartment electrochemical cell under an atmosphere of nitrogen. All measurements were carried out at a scan rate of  $100 \text{ mV s}^{-1}$  in the indicated solvent containing 0.1 m of Bu<sub>4</sub>NClO<sub>4</sub> or Bu<sub>4</sub>NB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub> as the supporting electrolyte. The working electrode was a homemade disk platinum electrode with a diameter of 2.0 mm. The electrode was polished prior to use with 0.05 µm alumina and rinsed thoroughly with water and acetone. A large-area platinum wire coil was used as the counter electrode. All the potentials are referenced to an Ag/AgCl electrode in saturated aqueous NaCl without regard for the liquid junction potential. Potentials versus ferrocene<sup>0/+</sup> can be estimated by subtracting 0.45 V.

**X-ray crystallography**: The X-ray diffraction data were collected by using a Rigaku Saturn 724 diffractometer on a rotating anode ( $Mo_{\kappa\alpha}$  radiation, 0.71073 Å) at 173 K. The structures were solved by direct methods using SHELXS-97<sup>[31]</sup> and refined with Olex2.<sup>[32]</sup> The structure graphics were generated by using Olex2.

CCDC-989554 (**3**), 989553 (**4**), and 989555 (**6**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

**Computational methods**: DFT calculations are carried out by using the long-range corrected hybrid functional CAM-B3LYP<sup>[33]</sup> implemented in the Gaussian 09 package.<sup>[34]</sup> The electronic structures of the complexes were determined by using a general basis set with  $6-31G^{*}$ .<sup>[35]</sup> Solvation effects in CH<sub>2</sub>Cl<sub>2</sub> were included in all calculations, and the conductor-like polarizable continuum model (CPCM) was employed.<sup>[36]</sup> No symmetry constraints were used in the optimization (nosymm keyword was used). Frequency calculations were performed with the same level of theory to ensure the optimized geometries were local minima. All the orbitals were computed at an isovalue of 0.02 e bohr<sup>-3</sup>.

**EPR spectroscopy**: EPR spectra were recorded on a Bruker ELEX-SYS E500-10/12 spectrometer at room temperature in  $CH_2CI_2$  solutions. The spectrometer frequency was  $9.7 \times 10^9$  Hz.

**Synthesis**: NMR spectra were recorded in the indicated solvent on a Bruker Avance 400 MHz spectrometer. Chemical shifts are reported in ppm values by using the residual protons of the deuterated solvent as reference. Mass spectra were recorded with a Bruker Daltonics Inc. Apex II FT-ICR or Autoflex III MALDI-TOF mass spectrometer. The matrix for MALDI-TOF measurement was  $\alpha$ -cyano-4hydroxycinnamic acid. Microanalysis was carried out by using a Flash EA 1112 or Carlo Erba 1106 analyzer at the Institute of Chemistry, Chinese Academy of Sciences.

**Synthesis of 1-(di-***p***-anisylamino)pyrene (1)**: A suspension of 1bromopyrene (100 mg, 0.36 mmol), di-*p*-anisylamine (122 mg, 0.53 mmol), tris(dibenzylideneacetone)dipalladium ([Pd<sub>2</sub>(dba)<sub>3</sub>], 16.0 mg, 0.018 mmol)], 1,1'- bis(diphenylphosphino)ferrocene (dppf, 9.9 mg, 0.018 mmol), and NaOtBu (41 mg, 0.43 mmol) in toluene (10 mL) was heated at 140 °C for 48 h under a N<sub>2</sub> atmosphere in a sealed pressure tube. The system was then cooled to room temperature. The solvent was removed under vacuum and the crude product purified by silica gel chromatography (eluting with petroleum ether/ethyl acetate, 120:1) to yield 72.0 mg of 1-(di-*p*anisylamino)pyrene (1) as a yellow solid in a yield of 47%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.77 (s, 6H), 6.78 (d, *J*=8.8 Hz, 4H), 7.00 (d, J=9.2 Hz, 4 H), 7.77 (d, J=8.0 Hz, 1 H), 7.92 (d, J=9.2 Hz, 1 H), 7.97 (t, J=7.6 Hz, 1 H), 8.03 (s, 2 H), 8.12 (m, 3 H), 8.19 ppm (d, J=9.2 Hz, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ =55.6, 114.7, 123.7, 123.8, 125.0, 125.1, 125.1, 126.0, 126.3, 126.5, 126.8, 126.9, 127.4, 127.5, 129.0, 131.2, 131.5, 142.2, 143.2, 154.8 ppm; HRMS (EI): calcd for C<sub>30</sub>H<sub>23</sub>NO<sub>2</sub> 429.1729; found: 429.1733.

Synthesis of 1,8-bis(di-p-anisylamino)pyrene (2): A suspension of 1,8-dibromopyrene (30 mg, 0.080 mmol), di-p-anisylamine (57 mg, 0.25 mmol), [Pd<sub>2</sub>(dba)<sub>3</sub>] (7.6 mg, 0.0080 mmol), dppf (4.6 mg, 0.0080 mmol), and NaOtBu (24 mg, 0.25 mmol) in 10 mL toluene was heated at 140  $^\circ\text{C}$  for 48 h under a  $N_2$  atmosphere in a sealed pressure tube. The system was then cooled to room temperature. The solvent was removed under vacuum and the crude product was purified by silica gel chromatography (eluting with petroleum ether/ethyl acetate, 60:1) to yield 19 mg of 1,8-bis(di-p-anisylamino)pyrene (2) as a yellow solid in a yield of 35%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.75 (s, 6H), 3.76 (s, 6H), 6.75 (m, 8H), 6.93 (d, J=8.8 Hz, 4H), 6.97 (d, J=9.2 Hz, 4H), 7.71 (d, J=8.4 Hz, 2H), 7.85 (d, J=9.2 Hz, 1 H), 7.96 (s, 1 H), 8.01 (s, 1 H), 8.02 (d, J=7.2 Hz, 1 H), 8.07 (d, J=8.0 Hz, 1 H), 8.11 ppm (d, J=9.2 Hz, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 55.5$ , 114.5, 120.5, 122.9, 123.2, 123.5, 123.6, 125.8, 125.9, 126.5, 126.6, 127.1, 127.3, 127.5, 127.7, 128.8, 129.1, 141.9, 142.0, 143.0, 154.6 ppm; MS (MALDI-TOF): m/z=656.3 [M]<sup>+</sup>; elemental analysis calcd (%) for C444H36N2O4•2H2O: C 76.28, H 5.82, N 4.04; found: C 75.92, H 6.25, N 3.89.

**Synthesis of 1,6-bis(di**-*p*-anisylamino)pyrene (3): Compound 3 was prepared from 1,6-dibromopyrene (100 mg, 0.28 mmol), di-*p*anisylamine (191 mg, 0.83 mmol), [Pd<sub>2</sub>(dba)<sub>3</sub>] (25 mg, 0.028 mmol), dppf (15 mg, 0.028 mmol), and NaOtBu (80 mg, 0.83 mmol) by using the same procedure as described for the synthesis of **2**. In this reaction, 133 mg of 1,6-bis(di-*p*-anisylamino)pyrene (**3**) was isolated as a yellow solid in a yield of 73%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ =3.76 (s, 12H), 6.76 (d, *J*=8.8 Hz, 8H), 6.97 (d, *J*=8.8 Hz, 8H), 7.71 (d, *J*=8.0 Hz, 2H), 7.85 (d, *J*=9.2 Hz, 2H), 8.02 (d, *J*=8.4 Hz, 2H), 8.10 ppm (d, *J*=9.2 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$ = 55.5, 114.6, 122.9, 123.5, 125.8, 126.6, 127.1, 127.3, 127.7, 128.8, 142.0, 143.0, 154.6 ppm; MS (MALDI-TOF): *m/z*=656.4 [*M*]<sup>+</sup>; elemental analysis calcd (%) for C<sub>44</sub>H<sub>36</sub>N<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O: C 78.32, H 5.68, N 4.15; found: C 78.23, H 5.58, N 4.24.

Synthesis of 1,3-bis(di-p-anisylamino)-7-tert-butylpyrene (4): Compound 4 was prepared from 1,3-dibromo-7-tert-butylpyrene(100 mg, 0.24 mmol), di-p-anisylamine (165 mg, 0.72 mmol), [Pd<sub>2</sub>(dba)<sub>3</sub>] (22 mg, 0.024 mmol), dppf (13 mg, 0.024 mmol), and NaOtBu (69 mg, 0.72 mmol) by using the same procedure as described for the synthesis of 2. In this reaction, 72 mg of 1,3-bis(dip-anisylamino)-7-tert-butylpyrene (4) was isolated as a yellow solid in a yield of 42 %.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCI}_3\text{):}~\delta\,{=}\,1.53$  (s, 9 H), 3.76 (s, 12H), 6.73 (d, J=9.2 Hz, 8H), 6.94 (d, J=8.8 Hz, 8H), 7.50 (s, 1 H), 7.82 (d, J=9.2 Hz, 2 H), 8.06 (d, J=9.2 Hz, 2 H), 8.07 ppm (s, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 13.7$ , 19.2, 29.7, 30.6, 31.8, 35.1, 53.4, 55.5, 65.5, 114.5, 114.6, 120.4, 122.1, 123.2, 123.2, 123.3, 123.4, 125.3, 126.8, 127.5, 128.8, 130.9, 131.2, 132.3, 142.5, 142.7, 149.5, 154.5 ppm; MS (MALDI-TOF):  $m/z = 712.3 [M]^+$ ; elemental analysis calcd (%) for C48H44N2O4·H2O: C 78.88, H 6.34, N 3.83; found: C 78.40, H 6.45, N 3.85.

Synthesis of 1,3,6-tris(di-*p*-anisylamino)pyrene (5) and 1,3,6,8-tetrakis(di-*p*-anisylamino)pyrene (6): A suspension of 1,3,6,8-tetrabromopyrene(100 mg, 0.19 mmol), di-*p*-anisylamine (266 mg, 1.16 mmol),  $[Pd_2(dba)_3]$  (27 mg, 0.029 mmol), dppf (16 mg, 0.029 mmol), and NaOtBu (111 mg, 1.16 mmol) in toluene (10 mL) was heated at 140 °C for 96 h under a N<sub>2</sub> atmosphere in a sealed pressure tube. The system was then cooled to room temperature and the solvent was removed under vacuum. The crude product

Chem. Eur. J. 2014, 20, 17454 - 17465



CHEMISTRY A European Journal Full Paper

was purified by silica gel chromatography (eluting with petroleum ether/ethyl acetate, from 7:1 to 3:2) to yield 27 mg of 1,3,6-tris(di*p*-anisylamino)pyrene (**5**) in a yield of 16% yield and 87 mg of 1,3,6,8-tetrakis(di-*p*-anisylamino)pyrene (**6**) in a yield of 40% as yellow solids.

Data for **5**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.74 (s, 18H), 6.71 (m, 12H), 6.91 (m, 12H), 7,49 (s, 1H), 7.66 (d, *J* = 8.2 Hz, 1H), 7.78(d, *J* = 9.1 Hz, 1H), 7.95 (s, 2H), 7.97 (d, *J* = 8.3 Hz, 1H), 8.05 ppm (d, *J* = 9.1 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 55.5, 114.5, 122.8, 122.9, 123.3, 123.5, 123.6, 125.7, 125.8, 125.9, 126.6, 126.9, 127.5, 127.9, 128.3, 128.5, 128.9, 129.2, 131.0, 141.8, 142.7, 143.0, 154.6 ppm; MS (MALDI-TOF): *m/z* = 883.2 [*M*-H]<sup>+</sup>; elemental analysis calcd (%) for C<sub>58</sub>H<sub>49</sub>N<sub>3</sub>O<sub>6</sub>·2H<sub>2</sub>O: C 75.71, H 5.81, N 4.57; found: C 75.97, H 5.85, N 4.30.

Data for **6**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 3.75 (s, 24 H), 6.71 (d, *J* = 8.6 Hz, 16 H), 6.89 (d, *J* = 8.8 Hz, 16 H), 7.47 (s, 2 H), 7.92 ppm (s, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 55.5, 114.5, 122.9, 123.3, 126.2, 128.5, 129.0, 142.5, 142.6, 154.6 ppm; MS (MALDI-TOF): *m/z* = 1110.2 [*M*]<sup>+</sup>; elemental analysis calcd (%) for C<sub>72</sub>H<sub>62</sub>N<sub>4</sub>O<sub>8</sub>: C 77.82, H 5.62, N 5.04; found: C 77.36, H 5.89, N 4.85.

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