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Steric effects on [4+4]-photocycloaddition reactions between complementary anthracene derivatives

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ABSTRACT

The steric effect of peripheral functional groups on the [4+4]-photocycloaddition between substituted anthracene derivatives was examined. The reactivity of 2,3,6,7-tetraphenylanthracene (**TPA**) with 2-phenylanthracene (**PA**), 2,9,10-trimethylanthracene (**TMA**) and 9,10-dimethyl-2,3-diphenylanthracene (**DMDPA**) was investigated. In all cases, the photodimers were formed in high yield despite the steric bulk of the peripheral substituents. It was further shown that although **PA** is capable of forming its homodimer, it selectively reacts with **TPA** when the latter is excited at 301 nm.

1. Introduction

Photochromism provides a versatile method for toggling molecular properties using light, and has been exploited in an enormous range of applications. Photochromic systems are most commonly based on unimolecular processes such as the trans-to-cis isomerisation of azobenzenes or the electrocyclization of diarylethene derivatives [1]. Although bimolecular processes such as the [4+4]-photocycloaddition of anthracene derivatives were amongst the first photochromic systems to be discovered, they have received much less attention than unimolecular switches [2–4]. Nonetheless, the last decade has witnessed a resurging interest in the photodimerization of anthracenes and related molecules, in part because they have the ability to bring together two molecules in a reversible fashion [5]. The [4+4]-photocycloaddition of anthracene has been used in applications that include [6–11] assembling and crosslinking of polymers, [12–15] modulating binding properties of receptors, [7,16] attenuating magnetic interactions [17–19] and patterning micro- and nano-structured materials [20–23].

Arguably one of the most attractive features of bimolecular reactions is the potential for bringing together two different molecules in a selective manner. Such selectivity is ubiquitous for many classes of thermal reactions, but has been largely unexplored in the context of [4+4]-photocycloadditions [5,15,24–26]. Hence, we have been investigating strategies for designing complementary pairs of anthracene derivatives, ***A*** and ***B***, capable of reacting with each other to form ***AB*** cyclomers to the exclusion of the ***AA*** and ***BB*** homodimers [27,28]. We have recently reported one such pair; irradiation of 9,10-dimethylanthracene (**DMA**) with 2,3,6,7-tetraphenylanthracene (**TPA**) afforded the cross-cyclomer, **DMA**–**TPA** as the exclusive product; the homodimers ***di*-TPA** and ***di*-DMA** were not observed (Scheme 1). This selectivity was rationalized in terms of the orthogonal steric demands placed on the two anthracene derivatives by their respective functional groups. Thus, the methyl groups on **DMA** and the phenyl groups on **TPA** effectively inhibit the formation of homodimers, but because these groups do not interact appreciably in **DMA**–**TPA**, they do not prevent the formation of this cross-cyclomer [27].

These observations prompted us to investigate the scope of selective cross-cyclization reactions, and in particular their tolerance with respect to the number and nature of substituents in the 2-, 3-, 6- and 7-positions. To this end, the photoreactivity of **TPA** with the three different anthracene derivatives, **TMA**, **PA**, and **DMDPA**, was examined. Both **TMA** and **DMDPA** possess methyl groups at the 9- and 10-positions, and are therefore not expected to form their homodimers. What was less clear was whether derivatives with a methyl or phenyl groups in the peripheral positions would show an appreciable tendency to react with **TPA**. The last derivative, 2-phenylanthracene (**PA**) lacks groups at the 9- and 10-positions, and is therefore expected to undergo homodimer formation; whether it could also react with **TPA**, and whether the latter process would be competitive with **PA** homodimerization were questions that we wished to address.

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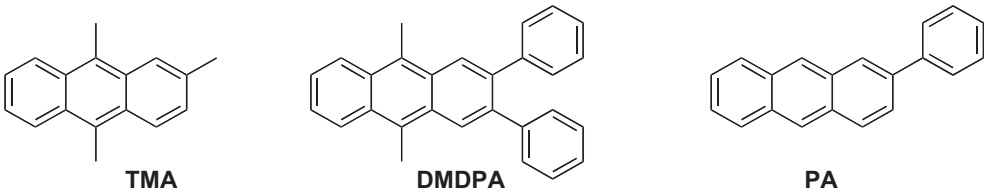


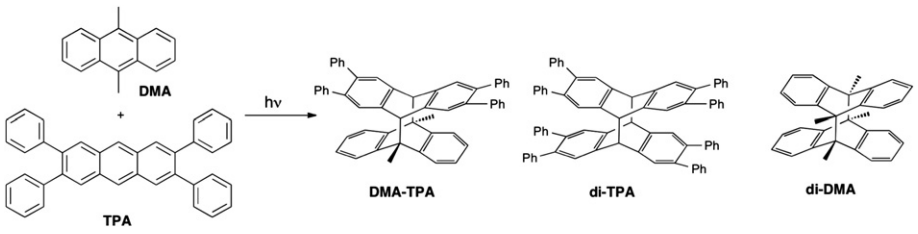
The syntheses of **TMA** and **DMDPA** are shown in Scheme 2. **TMA** was prepared from the reaction of 3-methylanthraquinone (**1a**) with methyl magnesium iodide to produce **2a**. This intermediate was not isolated; rather, it was treated *in situ* with a saturated solution of $HCl/SnCl_2$ to afford **TMA** in an overall yield of 30%. The same approach was employed to prepare **DMDPA** from 2,3-diphenylanthraquinone (**1b**); details of this synthesis have previously been reported from our group [28].

The synthesis of **PA** was accomplished in three steps from 2-aminoanthraquinone (**3**) using the approach shown in Scheme 3. Diazotization of **3**, followed by treatment with potassium iodide afforded 2-iodoanthraquinone (**4**), which was then coupled to phenylboronic acid under standard Suzuki coupling conditions to yield 2-phenylanthraquinone (5) in 74% yield. Reduction of this quinone to **PA** was accomplished using a two-step method in which the quinone was first treated with lithium aluminium hydride and aluminium chloride to afford **PA** as the major product, along with a small amount of the over-reduced product, 9,10-dihydro-2-phenylanthracene. Rather than attempt to isolate the desired product from this intractable mixture, the combined products were subjected to palladium on carbon to oxidize the dihydroanthracene side product to **PA**.

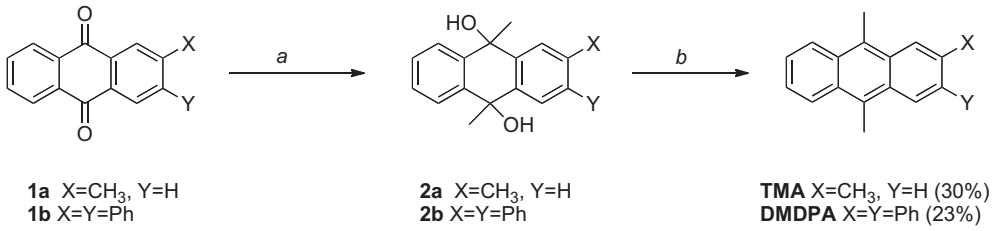
With the three anthracene derivatives in hand, we undertook to investigate their photochemical behaviour in the presence and absence of **TPA**. Our initial efforts focused on **TMA**, since this compound is structurally most similar **DMA**, which had previously been shown to react with **TPA**. No reaction was observed when a benzene solution containing only **TMA** was irradiated for 2 h using a Rayonet photoreactor with 300 nm lamps. This behaviour is similar to that of **DMA**, which also fails to undergo dimerization under these conditions [27,28]. Under similar conditions, anthracene forms its homodimer in 78% yield [27]. Thus, as expected, this 9,10-disubstituted compound shows little or no tendency to undergo [4+4]-photocycloaddition with itself.

In contrast, irradiation of a solution containing 4 mM of **TMA** and 4 mM **TPA** affords a single photoproduct. This product was examined by removing the solvent from the reaction mixture in vacuo; the residue was then redissolved in deuterated chloroform. The ^1H NMR of the photoproduct exhibited several new peaks in the aromatic region. Due to significant overlap of these peaks with each other and those of the starting materials, intepretation based on the aromatic peaks was difficult. However, four additional singlets were observed at 3.97 ppm, 2.13 ppm, 2.10 ppm and 2.09 ppm with relative integrations in a ratio of 2:3:3:3. The observation of these four new peaks is consistent with the formation of the photocyclomer **TPA**–**TMA** (Fig. 1). The peak at 3.97 ppm was assigned to the protons *a* and *a′* originating from the **TPA** fragment, and is similar to the chemical shift observed for the corresponding protons in **DMA**–**TPA**, which appear at 4.08 ppm [27]. Although not formally chemically equivalent, it is anticipated that *a* and *a′* should exist in virtually identical chemical environments, and therefore exhibit coincident chemical shifts. The remaining peaks in the vicinity of 2.1 ppm were assigned to the methyl protons *c*, *d* and *e*. These peaks are all considerably shifted relative to those in the parent compound **TPA**, which appear at 3.08, 3.07 and 2.59 ppm. The observed shifts for the methyl protons at the 9- and 10-position are similar to those seen in the case of **DMA**–**TPA**, which shift from 3.11 ppm in **DMA** to 2.19 ppm in the cyclomer. Such as shift is to be expected, since the carbons adjacent to the methyl groups change from sp^2 to sp^3 hybridization. The upfield shift observed for the methyl protons *e* is likely due to the protons being shielded by the close proximity of the phenyl rings from **TPA**.

Based on these assignments and the relative integrations of the identifiable (*i.e.* non-aromatic) peaks from both the starting materials and the product, the yield of **TPA**–**TMA** was estimated to be approximately 68%. In comparison, **TPA**–**DMA** was obtained in 65% yield under similar reactions conditions (300 nm, 4 mM **TPA**, 4 mM **DMA**, 140 min), suggesting that the steric hindrance between the peripheral methyl group at the 2-position of **TMA** and the phenyl groups of **TPA** is not sufficient to significantly impede reaction between these two chromophores. The extent to which the steric demands of the methyl group impact on the ability of **TMA** to undergo photocyclomerization is difficult to ascertain, since the yield of product will depend on a variety of factors, including the degree of photo- and thermal-reversion during the experiment and on the excited state populations of both molecules under the irradiation conditions. The excited state population of **TMA** will, for example, depend on both how much light it absorbs and its excited state lifetime. We have not at this time carried out experiments to determine the extent to which these factors play in the efficiency with which **TMA** is able to react with **TPA**. Nonetheless, the present observations are encouraging, as they indicate that our complementary chromophore strategy is relatively tolerant towards functionalization at the 2-position of 9,10-dimethylanthracene derivatives. It may be possible to exploit this in order to incorporate these chromophores into functional materials (e.g. polymers, surfaces or nanoparticles) via linking groups at the 2-position. We did not observe thermal decomposition of **TPA**–**TMA** during the



Scheme 1. Selective photocycloaddition of **TPA** and **DMA** to form **DMA**–**TPA** as the exclusive product. Homodimers ***di*-DMA** and ***di*-DMA** were not observed.



Scheme 2. Reagents and conditions: a) Mg, CH_3I, Et_2O, reflux; b) $SnCl_2$, HCl(aq), RT.

course of our experiments, suggesting that 2-methyl group does not appreciably destabilize the photoproduct.

Similar results are obtained when we examined **DMDPA**. As noted elsewhere [28], no photoproduct is observed when this compound is irradiated by itself in solution. However, exposing a benzene solution containing 4 mM **DMDPA** and 4 mM **TPA** to 350 nm light for 100 min led to the formation of a single photoproduct with diagnostic peaks in the ^{1}H NMR at 4.12 ppm and 2.23 ppm, which were assigned as the protons a and *b* of **TPA**–**DMDPA** (Fig. 2). The chemical shifts of these peaks are in excellent agreement with 4.08 and 2.19 ppm peaks of **TPA**–**DMA** (*vide supra*). Based on the relative integration of these peaks and those of the starting compounds, the yield of this product was estimated as 64%. Remarkably, then, it appears that even two relatively large phenyl groups at the 2- and 3-positions of a 9,10-dimethylanthracene chromophore will still permit these compounds to readily undergo photodimer formation.

Attempts to characterize this photoproduct by CI mass spectrometry yielded only two peaks at m/z = 359 and 483, which correspond to the M+1 peaks for **DMDPA** and **TPA**, respectively. This result is not entirely unexpected, as anthracene photodimers commonly fragment to their monomers in mass spectrometry experiments [2]. Thus, while these experiments cannot unambiguously confirm the identity of the photoproduct as **DMDPA**–**TPA**, the absence of peaks for other possible photoproducts, such as endoperoxides, does support the proposed structure.

The UV–visible absorption spectrum of this photoproduct exhibits a new band centred at 240 nm (Fig. 3b); the sample also exhibits peaks for residual monomers **TPA** and **DMDPA** (Fig. 3a), which absorb at longer wavelengths. The shorter wavelength of absorption for the photoproduct is consistent with the decreased conjugation of the proposed dimer.

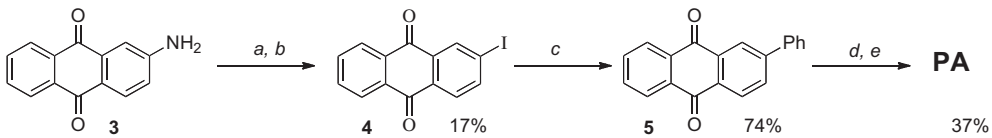
We next turned our attention to the reactivity of 2-phenylanthracene (**PA**). Unlike the other derivatives discussed so far, this compound lacks functional groups at the 9- and 10-positions, and therefore is likely to undergo photodimerization on its own. Indeed, the closely related 2,3-diphenylanthracene readily forms its photodimer [28]. This conjecture was borne out by the observation that irradiation of an 8 mM solution of **PA** in a Rayonet for 90 min (350 nm lamps) led to the formation of a number of photoproducts characterized by multiple ^{1}H NMR peaks in the range 4.64–4.21 ppm, consistent with the protons at the sp^3-hybridized carbons of the photodimers. In this case, multiple photoproducts are observed because of the possibility for a variety of regioisomers being formed. Using the cumulative integration of the peaks in this region and the integration for the 9- and 10-protons of **PA**, it was estimated that this compound underwent 90% conversion under these conditions.

Several additional, poorly resolved peaks are observed in the range 4.68–4.67 ppm when a solution of 4 mM **PA** and 4 mM **TPA** were irradiated under the same conditions; in fact, these peaks appear to represent the major product (~55%), which is proposed to be the cyclomer **TPA**–**PA**. The homodimers are also in evidence (~25%). It therefore appears that cross-cyclomer formation is able to compete with **PA** homodimer formation.

As already noted, further characterization of the photoproduct by mass spectrometry is complicated by the tendency of photodimers to decompose to monomeric fragments. In the case of the photoproduct formed upon irradiation of **TPA** and **PA**, only a peak associated with M+1 for **PA** was observed. Although our assignment of this photoproduct as **TPA**–**PA** must therefore be treated with caution, the failure to observe peaks other than those of the monomer is consistent with the product being a dimer rather than another photoproduct such as an endoperoxide.

The ability of **TMA** and **DMDPA** to only form their respective cross-cyclomer products with **TPA** relies, as already noted, on their inability to homodimerize under the conditions examined. These considerations at first glance seem to preclude **PA** from exhibiting similar exclusivity, since, if excited, this compound does form its dimer. However, we have recently shown [28] that specificity for the cross-cyclomer can also be enforced even in cases where one of the components is capable of forming its homodimer simply by not exciting that molecule. This is accomplished by selective irradiation of the component that is unable to form its homodimer. In this manner, it was demonstrated that the cross-cyclomer of anthracene and **TPA** could be formed as the exclusive product when **TPA** was excited at wavelengths where anthracene had a negligible absorbance [28].

We therefore decided to investigate whether this approach could be extended to **PA**. The UV–visible spectra of **TPA** and **PA** are shown in Fig. 4. An important feature in the comparison of these spectra is the strong absorbance band for **TPA** at 301 nm, a region in which **PA** has negligible absorbance. When **TPA** was selectively excited at this wavelength in the presence of **PA**, only the peaks associated with the cross-cyclomer were observed; the homodimer peaks were not in evidence. Under the conditions used to carry out selective irradiation, the product identified as **TPA**–**PA** was formed in an estimated 8% yield. The lower yield in this case may be ascribed to the much lower irradiation levels in this experiment, which used a fluorimeter as the light source, versus experiments carried out in a Rayonet.



Scheme 3. *Reagents and conditions:* a) $NaNO_2$, HCl, H_2O, 5 °C; b) KI, H_2O, RT; c) phenylboronic acid, Na_2CO_3, H_2O, 1,2-dimethoxyethane, cat. $PdCl_2(PPh_3)_2$; d) LiAlH3, $AlCl_3$, THF; e) Pd/C, xylenes.

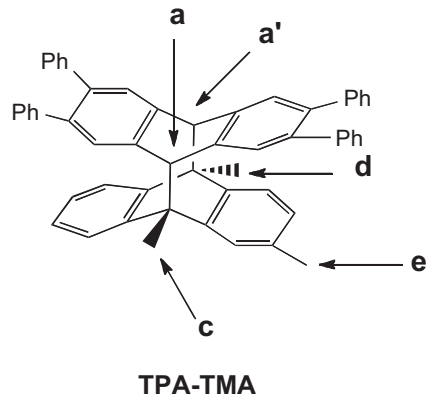


Fig. 1. Proposed structure of photoproduct formed from irradiation of a solution of **TPA** and **TMA**.

2. Conclusion

Our results indicate that although the bulky phenyl substituents on **TPA** inhibit its ability to homodimerize, they do not preclude its reaction with other anthracene derivatives bearing groups in the 2- and 3-positions. This suggests that a broader range of molecules can act as complementary pairs in [4 + 4]-photocycloaddtion reactions. Most importantly, 9,10-dimethylanthracene derivatives, which show almost no tendency to homodimerize, can be functionalized at the 2-position without appreciably diminishing their ability to react with **TPA**-like derivatives. This opens the door to creating molecules that are complementary and functional, in which **DMA** derivatives are attached via the 2-position to receptors, catalysts, nanoparticles or polymers. We are actively pursuing these possibilities.

3. Experimental

3.1. Materials and methods

^{1}H NMR spectra were obtained using a Bruker AMX-400 400 MHz spectrometer. Melting Points were determined either on a Fisher Johns Melting Point Apparatus and are uncorrected. UV–visible spectrometry was performed on a Cary 100 UV–Vis spectrophotometer. Selective irradiation experiments on TPA/PA were carried out on a PTI C60 Photon Counting Spectrofluorimeter.

Compound **1a** and **3** were obtained from Aldrich Chemical Co. and used without further purification. Anthraquinone **1b** was prepared according to previously reported methods [29]. Benzene, aluminum trichloride, lithium aluminum hydride, hexanes and toluene were purchased from Anachemia. Palladium on carbon (10% Pd/C) was purchased from Aldrich Chemical Company. Xylenes, THF and anhydrous $MgSO_4$ purchased from Caledon Laboratories Ltd. 230–400 mesh ASTM silica gel was purchased from EMD Chemicals Inc. Chemical ionization mass spectrometry experiments were carried out on a Varian 4000 GC/MS/MS mass spectrometer.

Non-selective irradiation experiments were performed under a nitrogen atmosphere in glass Schlenk tubes. These experiments were carried out in a Rayonet fitted with ten 300 or 350 nm lamps, as specified. In a typical experiment, a 2.5 ml benzene solution containing 4 mM of each chromophore was subjected to three freeze–pump–thaw cycles in order to ensure the exclusion of oxygen from the reaction mixtures. After irradiation for 2 h, the solvent was removed in vacuo and the ratio of the products was determined by

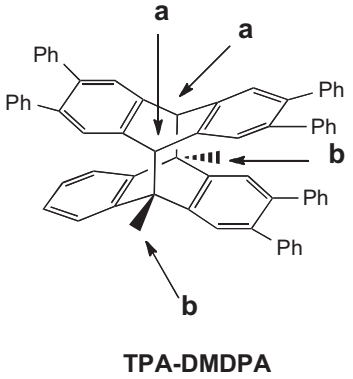


Fig. 2. Proposed structure of the photoproduct obtained from irradiating **TPA** and **DMDPA**.

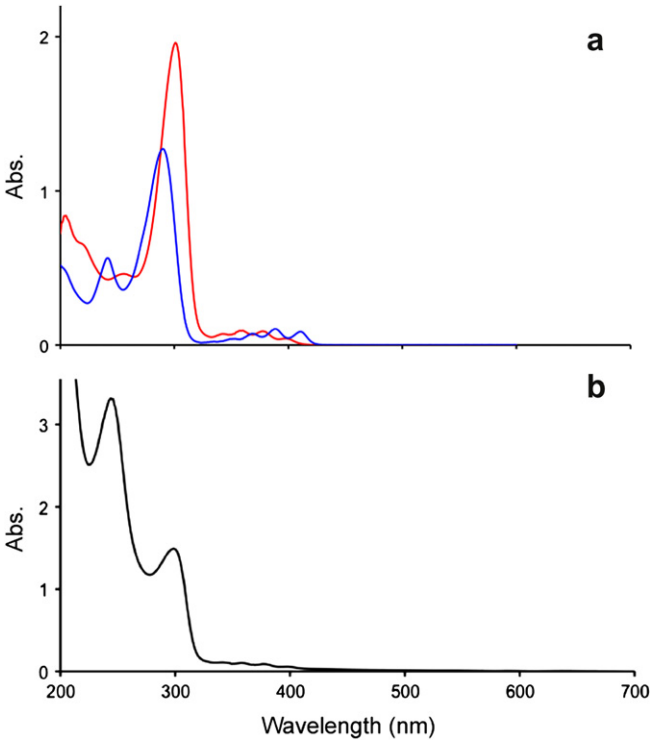


Fig. 3. UV–visible absorption spectra of (a) **TPA** (solid) and **DMDPA** (dashed) and (b) photoproduct **TPA**–**DMDPA** in acetonitrile. Note that the ^{1}H-NMR of the photoproduct indicates the presence of **TPA** and **DMDPA** in the sample used for spectrum b.

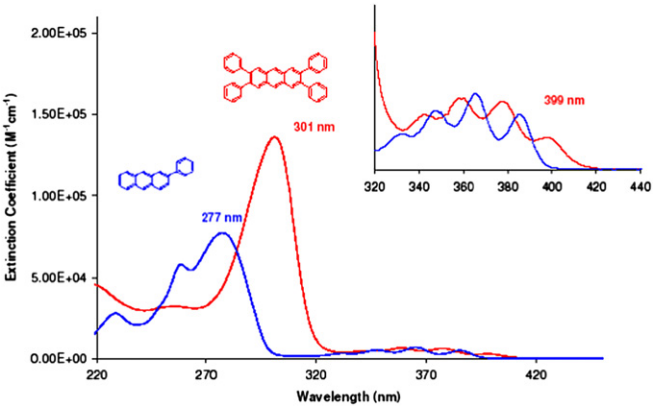


Fig. 4. UV–visible absorption spectra of **TPA** and **PA** in acetonitrile.

^{1}H NMR. Selective irradiation experiments were carried out in deoxygenated $CDCl_3$ solutions in quartz NMR tubes and using a spectroflourimeter as the light source (slit width = 5 nm) using a 1 ml solution containing 10 mM of **TPA** and 10 mM **PA**.

2-Iodoanthraquinone (4) 2-Aminoanthraquinone (5 g, 22.3 mmol) was suspended in a mixture of 15 ml HCl and 15 ml ice. In a separate container 2.7 g (40 mmol) of $NaNO_2$ was dissolved in 15 ml of H2O. While maintaining the 2-aminoanthraquinone solution in an ice bath the $NaNO_2$ solution was added slowly over a 20-min period. This solution was then allowed to stir for another 1 h at 5 °C and then carefully poured into a solution of KI (6.6 g, 40 mmol) in 50 ml of H_2O and allowed to stir for a further 30 min. The crude product was then sublimed under vacuum to yield 1.3 g (3.9 mmol, 17%) of the pure 2-iodoanthraquinone. ^{1}H NMR: (ppm) (CDCl3) 8.64 d (1H, J = 1.8 Hz), 8.30 m (2H), 8.15 dd (1H, J = 1.8 Hz, J = 8.2 Hz), 7.99 d (1H, J = 8.2 Hz), 7.82 dd (2H, J = 3.3 Hz, J = 5.8 Hz); mp: 173–175 °C, lit. 175–176 °C [30].

2-Phenylanthraquinone (5) To a Schlenk flask, 500 mg (1.5 mmol) of 2-iodoanthraquinone, 270 mg (2.25 mmol) of phenylboronic acid, 1.85 g (15 mmol) of $Na_2CO_3{\cdot}H_2O$, 20 mg (0.03 mmol) of $PdCl_2(PPh_3)_2$ were added to 10 ml H_2O and 4 ml 1,2-dimethoxyethane. This solution was sealed and heated to 80 °C for 48 h. The solution was then cooled to RT, and poured into Et_2O and H_2O (30 ml each). The organic layer was separated and the aqueous layer was extracted with Et_2O (3 × 30 ml). The combined ethereal extracts were dried over $MgSO_4$ and concentrated in vacuo resulting in the desired product in 74% yield (470 mg, 1.65 mmol). This product was used without further purification. ^{1}H NMR: (ppm) ($CDCl_3$) 8.55 d (1H, J = 1.9 Hz), 8.39 d (1H, J = 8.1 Hz), 8.35 m (2H), 8.03 dd (1H, J = 1.9 Hz, J = 8.1 Hz), 7.82 dd (1H, J = 1.2 Hz, J = 2.5 Hz), 7.82 d (1H, J = 9.1 Hz), 7.74 d (2H, J = 7.1 Hz), 7.53 t (2H, J = 7.3 Hz), 7.47 dt (1H, J = 4.7 Hz, J = 1.9 Hz); mp: 162–164 °C, lit. 163–164 °C [31].

2-Phenylanthracene (PA) In an oven-dried 100 mL Schlenk tube, 2-phenylanthraquinone (300 mg, 1.06 mmol) was dissolved in 20 ml dry tetrahydrafuran cooled to −78 °C in a dry ice/acetone bath. To this solution 500 mg (3.8 mmol) of lithium aluminum hydride and 875 mg (18.8 mmol) of aluminum trichloride were carefully added, this mixture was then allowed to warm to room temperature and heated at reflux for 24 h under N_2. The solution was then cooled and poured into diethyl ether (50 ml) and carefully quenched with water (50 ml). After extraction with three further portions of diethyl ether (50 ml each) the ethereal extracts were dried with magnesium sulfate, and finally concentrated in vacuo. This crude product was then dissolved in 50 ml xylenes and 420 mg Pd/C was added to the solution, which was then heated at reflux for 9 days. The product was then cooled to room temperature and eluted through a plug of SiO_2 with toluene. This resulted in the 170 mg of the desired product, which was recrystallised from acetone yielding 100 mg (0.39 mmol, 37%) of the desired product as a yellow solid. ^{1}H NMR: (ppm) (CDCl3) 8.48 s (1H), 8.45 s (1H), 8.21 s (1H), 8.09 d (1H, J = 8.9 Hz), 8.02 dd (1H, J = 1.2 Hz, J = 4.3 Hz), 8.02 d (1H, J = 9.7 Hz), 7.75–7.80 m (3H), 7.51 t (2H, J = 7.6 Hz), 7.47 dd (^{1}H, J = 1.1 Hz, J = 3.4 Hz), 7.47 d (1H, J = 9.7 Hz), 7.40 tt (1H, J = 7.4 Hz, J = 1.2 Hz); UV–Vis: λ_{max} = 277 nm (ε = 77,000 $M^{-1}cm^{-1}$); mp: 206–207 °C, lit. 207–208 °C [32].

2,9,10-Trimethylanthacene (TMA) In an oven-dried 100 mL round bottom flask kept under N_2, 40 mL of dry diethyl ether was charged with 240 mg (10 mmol) of ground magnesium shavings. To this was added 0.6 mL (10 mmol) of methyl iodide. Once the Grignard reagent had formed (as indicated by consumption of visible magnesium shavings) 300 mg (1.35 mmol) of 2-methylanthraquinone was added. The solution was heated at reflux for 42 h, then cooled and 55 mL of a 10% HCl solution saturated with $SnCl_2$ was added and allowed to stir for a further 20 h at room temperature. This solution was then diluted with water (75 ml) and extracted with diethyl ether (3 × 75 ml). After drying the ethereal layer with magnesium sulfate, the solution was concentrated in vacuo. This crude product was then directly applied to a silica gel column and eluted with a mixture of hexanes and toluene (9:1) 90 mg (41 mmol, 30%) of the desired product was recovered as a yellow solid. ^{1}H NMR: (ppm) ($CDCl_3$) 8.32–8.30 m (2H), 8.24 d (2H, J = 9.0 Hz), 8.07 s (1H), 7.47–7.50 m (2H), 3.08 s (3H), 3.07 s (3H), 2.59 s (3H); mp: 97 °C, lit. 96 °C [33].

TPA–TMA ^{1}H NMR (ppm) ($CDCl_3$) 7.20–6.85 m (45H), 3.97 s (2H), 2.13 s(3H), 2.10 s (3H), 2.09 s (3H)

TPA–DMDPA ^{1}H NMR (ppm) ($CDCl_3$) 7.17–6.93 m (40H), 4.12 s (2H), 2.23 s (6H).

TPA–PA ^{1}H NMR (ppm) ($CDCl_3$) 7.18–6.81 m (54H), 4.682, 4.677, 4.671 (poorly resolved singlet's, 4H).

Acknowledgments

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