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Soluble Tetraaminotriptycene Precursors

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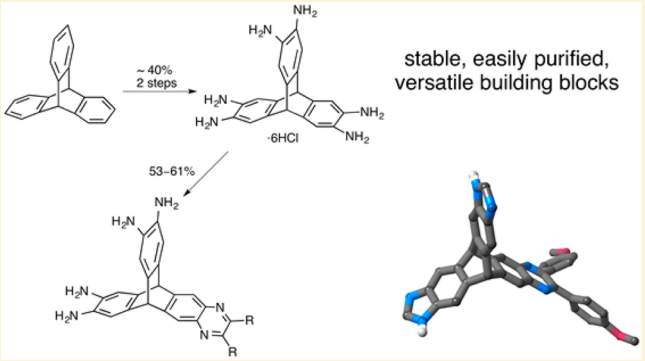
Supporting Information

ABSTRACT: An efficient route to soluble triptycene tetraamines, shape-persistent molecules containing two *ortho*-phenylenediamine motifs, is reported. These tetraamines are stable, prepared in good yields, easily purified by column chromatography, and can be readily condensed to give a range of imidazole and pyrazine derivatives.



Triptycene and its derivatives are a class of rigid, shape-persistent organic molecules containing three aromatic rings attached to a central bridgehead motif. These compounds have found widespread use as building blocks in supramolecular and materials chemistry,[1−4] for example, in the synthesis of conjugated polymers,[5−7] molecular rotors,[8,9] interlocked structures,[10−12] and cage molecules.[13−15]

Triptycenes incorporating phenyl rings functionalized with *ortho*-diamine groups are valuable precursor molecules, as the phenylenediamine moieties readily condense with carbonyl-containing compounds to give a variety of heterocyclic functionalities, as well as metal−salphen complexes. Tris-phenylenediamine functionalized triptycene (i.e., 2,3,6,7,14,15-hexaaminotriptycene,[16] or its hexahydrochloride[17] salt) has proven to be a versatile compound to prepare a range of interesting materials, including porous organic crystals[18] and polymers,[19−21] metal organic frameworks,[16] and porous[22] or catalytically active metal complexes.[23]

Building blocks where two of triptycene's phenyl rings are functionalized are of interest to us, either as precursors to cleft-like dinuclear metal complexes[24] that may display interesting catalytic properties or as synthons for the synthesis of large, hexagonal, belt-like macrocycles.[25] In this work, we report a quick and efficient route to a family of soluble triptycene bis-phenylenediamine compounds and demonstrate their use as general synthons by conversion to several heterocycle-containing derivatives.

The only known synthesis of a bis-diamino triptycene is a preliminary report from our group. We prepared the parent bis-diamino compound 2,3,6,7-tetraaminotriptycene and used it to synthesize bis-phenanthroline-modified triptycene.[26] We have now optimized the synthesis of tetraaminotriptycene, which is prepared as its tetrahydrochloride adduct using a nitration, reduction, acetylation, nitration, deprotection, and reduction strategy starting from triptycene (Scheme 1). The only difficulty with this procedure came when trying to prepare known dinitrotriptycene **1**. This compound has previously been prepared using concentrated nitric acid in acetic anhydride,[27−29] but we found that this procedure gave primarily mononitro- or trinitrotriptycene, with very little dinitrotriptycene isolated. Instead, we found that Mellor et al.'s nitration conditions[30] using cerium ammonium nitrate and sulfuric acid in dichloromethane readily gave a mixture of 2,6- and 2,7-dinitrotriptycene in 56% yield after optimization (see the Supporting Information). Subsequent reduction gave a mixture of isomers of diaminotriptycene, which were acetylated *in situ* and then nitrated at the other *β*-position to give two isomers of 2,3,6,7-dinitrodiacetamidotriptycene **2**. Deprotection of the acetyl groups using hydroxide gave diaminodinitrotriptycene **3**, which was reduced using $SnCl_2{\cdot}2H_2O$ in $EtOH/HCl_{(aq)}$ to give 2,3,6,7-tetraaminotriptycene tetrahydrochloride **4·4HCl**. This compound was isolated as a crystalline air-stable solid, after purification by recrystallization, with an overall yield of 20% from triptycene.

While **4·4HCl** can be prepared on large scales, we have found that it is a far from ideal starting material, both in terms of the number of synthetic steps required to prepare it and because exploratory studies showed that compounds derived from this tetraamine show poor solubility (e.g., triptycene bis-imidazole **5**, which shows significant solubility only in very polar organic solvents such as DMF and DMSO). While it may be possible to add solubilizing groups to triptycene, for example, by cross-coupling reactions of 2,3-dibromotriptycene, followed by successive installation of the diamino groups (using a similar strategy to that shown in Scheme 1), this would further extend an already lengthy synthesis. Instead, we have developed the selective functionalization of one of the three

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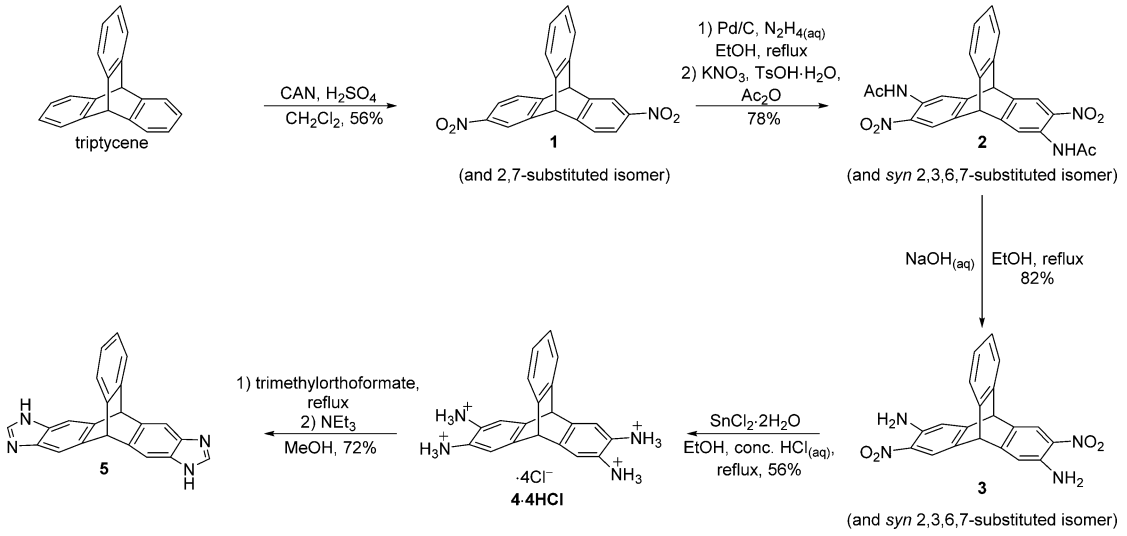
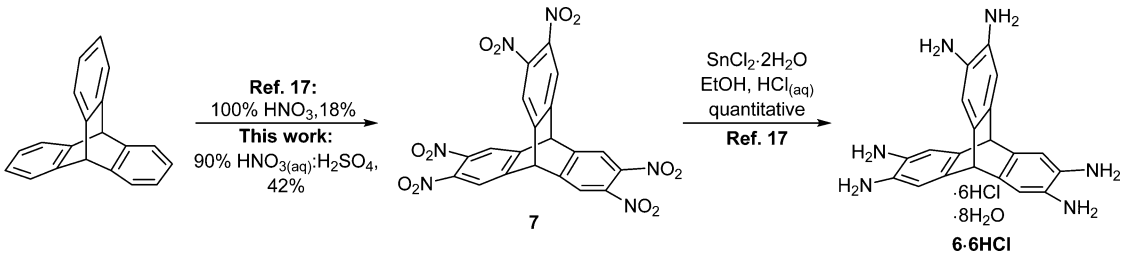
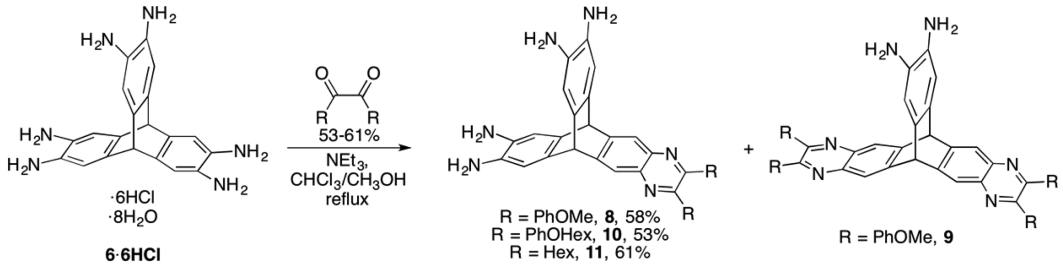
Scheme 1. Synthesis of Tetraamine 4·4HCl and Its Conversion to Bis-imidazole 5



Scheme 2. Mastalerz et al.'s[17] and Our New Syntheses of Hexanitrotriptycene, and Subsequent Reduction to 6·6HCl



Scheme 3. Synthesis of Solubilized Triptycene Tetraamines



phenylenediamine groups of readily prepared hexaaminotriptycene **6**, to both introduce a solubilizing group and leave a bis-phenylenediamine (i.e., tetraamine) precursor in one synthetic step.

In order for this this strategy to be effective, we needed an efficient and high yielding synthesis of hexaaminotriptycene. Several routes to this precursor have been reported (see Scheme S1):[16,17,19] we deemed Mastalerz et al.'s procedure[17] to be the most attractive as it offers a route to the air-stable hexahydrochloride adduct of hexaaminotriptycene in only two steps, without the need for chromatographic purification (Scheme 2). The drawbacks of this method are the use of highly hazardous 100% nitric acid in the nitration step and the low yield of hexanitrotriptycene **7** (18%). We have found that using a mixture of 90% $HNO_{3(aq)}$ and H_2SO_4 at 85 °C gives nearly complete conversion to hexanitrotriptycene, of which approximately 60% is the desired all-β isomer **7** and the remainder appears to mainly consist of other isomers (as determined by ^{1}H NMR analysis of the crude reaction mixture; see Figure S4). Recrystallization from boiling acetone gave nearly pure **7** (Figure S6) in 42% yield. Subsequent treatment with $SnCl_2{\cdot}2H_2O$, according to Mastalerz et al.'s procedure,[17] yielded pure 2,3,6,7,14,15-hexaaminotriptycene hexahydrochloride (**6·6HCl**), which analyzed as the octahydrate.[31] We found that any side products arising from traces of impurity in **7** are removed during workup as they remain dissolved in the EtOH/$HCl_{(aq)}$ reaction mixture, from which the product is isolated by filtration. Overall, this procedure provides rapid access to gram quantities of clean **6·6HCl**.

With a convenient and high-yielding synthesis of hexaamino precursor **6·6HCl** in hand, we investigated methods to add solubilizing substituents to one of the three phenylenediamine rings. Finding suitable reaction conditions was nontrivial, as **6·6HCl** is only soluble in highly polar organic solvents (DMF and DMSO), while neutralizing gives the free-base, which is much more soluble, but prone to rapid decomposition. However, it was found that **6·6HCl** could be finely dispersed in methanol by sonication; addition of anisil (4,4′-dimethox-

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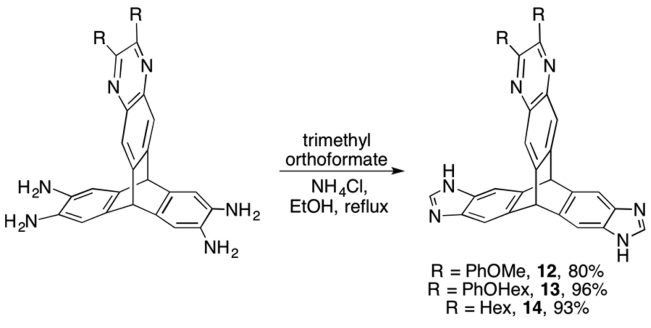
ybenzil) and triethylamine (in excess) in chloroform, followed by reaction at reflux temperature, gave the solubilized tetraaminotriptycene **8** in 58% yield (Scheme 3).

Best results were obtained when 2 molar equiv of **6·6HCl** were used, to disfavor formation of doubly and triply reacted products. Excess hexaaminotriptycene (and/or its decomposition products) was easily removed by evaporating the reaction mixture to dryness, suspending the brown solid in dichloromethane, and filtering through Celite to give a yellow solution, which ^{1}H NMR analysis showed contained mainly the desired product **8**, as well as a smaller amount of the doubly reacted side-product **9**. These could be readily separated by silica gel column chromatography giving **8** and **9** in 58% and 19% isolated yield, respectively (yield based on anisil). We also found that **9** could be prepared deliberately in 48% yield by reacting 1 equiv of **6·6HCl** with 2 equiv of anisil. While we have not attempted to optimize this procedure, we note that this three-step synthesis (from triptycene) is a much shorter route to 2,3-diaminotriptycenes than that previously reported (five steps).[16] Additionally, the product incorporates additional functionality, which may be used to modify the solubility and other properties of the molecules.

We reacted **6·6HCl** with a range of 1,2-diketones; 4,4′-dihexyloxybenzil or 7,8-tetradecanedione smoothly gave **10** and **11**, which were isolated in 53% and 61% yield, respectively. When smaller diketones (2,3-butadione or 2,3-dihydroxydioxane, a masked glyoxal) were used, yellow powders precipitated from the reaction mixture. These were shown by ^{1}H NMR spectroscopy (in DMSO-d_6) to be reasonably pure (85−90%; see Figures S1 and S2) tetraamine products. Unfortunately, these mixtures displayed poor solubility and were not easily purified by column chromatography or recrystallization. Given our aim was to prepare soluble tetraamine precursors, we did not explore this further. Perhaps surprisingly, the tetraamines appear to be relatively stable in their neutral form (free-base hexaaminotriptycene **6** decomposes rapidly in air): we found no significant change in the ^{1}H NMR spectra of these compounds after storing them in CD_2Cl_2 for a week,[32] or in a vial in a −20 °C freezer for several months. Storing in a vial on the benchtop at room temperature for several weeks appears to cause minor decomposition (as evidenced by a change in color from orange to brown), although this was barely detectable by ^{1}H NMR spectroscopy.

We next studied the reactivity of the new tetraamines: reaction with excess trimethyl orthoformate in refluxing ethanol in the presence of ammonium chloride gave smooth conversion to the triptycene bis-imidazoles **12**−**14** in 80−96% isolated yields (Scheme 4), showing that the addition of the solubilizing substituent does not appear to deleteriously affect the reactivity of the tetraamines. We were able to obtain single crystals of **12** and structurally characterize the molecule by X-ray crystallography (Figure 1).[33] The molecule packs through short hydrogen bonds between one of the imidazole rings and the pyrazine group (H···N = 2.02 and 2.11 Å, 71% and 74% of the sum of the van der Waals radii[34] of H and N), while the other imidazole heterocycle hydrogen bonds to solvent molecules.

Scheme 4. Synthesis of Substituted Triptycene Bis-imidazoles from Tetraamines



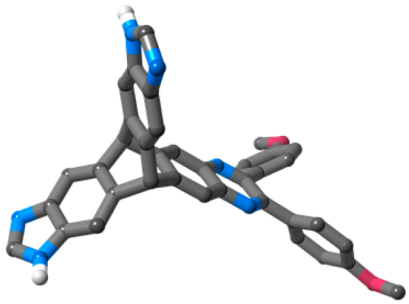


Figure 1. Solid-state structure of triptycene bis-imidazole **12** as determined by single-crystal X-ray diffraction. Solvent molecules and most hydrogen atoms omitted for clarity.

Heating the methoxyphenyl-substituted tetraamine, **8**, to reflux with diketones in 1:1 chloroform:methanol gave smooth conversion to a range of pyrazine derivatives in 77−85% yield (Scheme 5). Using this approach, we were able to prepare a tris-triptycene molecule **16**, a pyrene-substituted derivative **17** that displays interesting photophysical properties (see the Supporting Information), and compounds containing transition-metal-binding motifs.[35] These compounds demonstrate the diverse range of materials that can be prepared from the new tetraamine building blocks.

In summary, we have improved the synthesis of hexanitrotriptycene and used this as the basis of a facile route to soluble tetraaminotriptycenes (containing two phenylenediamine motifs). These tetraamines show surprisingly good stabilities, can be readily purified by column chromatography, and are versatile building blocks for functional heterocycle-containing derivatives.

EXPERIMENTAL SECTION

General Remarks. Anisil was prepared following a literature procedure,[36] bis(hexyloxy)benzyl was prepared from anisil according to the literature procedure,[37] and 7,8-tetradecanedione was prepared following the method of Marchese and co-workers.[38] Di-^{t}Bu-pyrene dione[39] and triptycene quinone[40] were prepared by oxidizing di-^{t}Bu-pyrene[39] and dimethoxytriptycene,[41] respectively, as previously described. Hexaaminotriptycene·6HCl·nH$_2$O was prepared by reducing hexanitrotriptycene **7** with $SnCl_2·2H_2O$ as described previously.[17] All other reagents and solvents were bought from commercial suppliers and used as received.

Triptycene. Triptycene is commercially available from several suppliers, but is still expensive. Numerous syntheses of triptycene have been reported[42] in yields of up to 86%. The following procedure is a modification of that reported by Friedman and Logullo,[43] which is not as high yielding but gives reproducibly quick and easy access to large quantities of triptycene from inexpensive starting materials.

Anthracene (17.8 g, 100 mmol) was dissolved in refluxing 1,2-dichloroethane (400 mL). At reflux, under a nitrogen atmosphere, isopentyl nitrite (16.1 mL, 14.1 g, 120 mmol) was added in one portion, followed by anthranilic acid (15.1 g, 110 mmol) in 1,2-dimethoxyethane (150 mL) dropwise over approximately 1 h. Once addition was complete, the reaction was heated at reflux for a further

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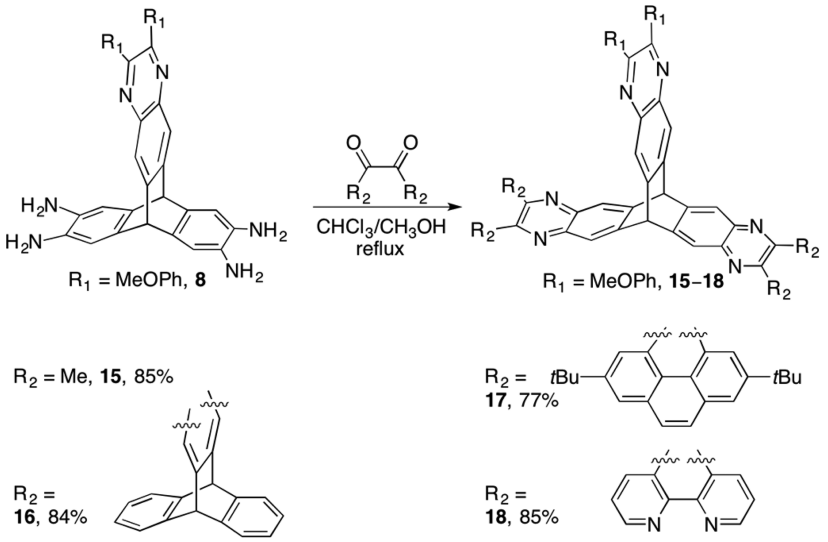
Scheme 5. Synthesis of Triptycene Bis-pyrazine Derivatives



30 min and then taken to dryness under reduced pressure. Maleic anhydride (9.82 g, 100 mmol) and 1,4-dioxane (100 mL) were added to the brown solid, and the suspension was heated to reflux for 1 h, during which time all material dissolved. The reaction was cooled to room temperature and poured into a mixture of methanol (500 mL), water (500 mL), and KOH (50 g), which was cooled in an ice-bath. The resulting pale brown suspension was stirred for 5 min and then filtered. The solid was washed with 4:1 methanol:water (4 × 100 mL) to give a sand-colored powder. This was taken up in warm butanone (150 mL), filtered hot, and poured into methanol (600 mL). The resulting brown solution was cooled in a freezer, causing the precipitation of slightly off-white crystals. These were isolated by filtration and washed with cold methanol (3 × 30 mL) and cold pentane (2 × 20 mL). Yield: 12.2 g (48.0 mmol, 48%).

Additional crops of crystals could be obtained by concentrating the mother liquor, dissolving the resulting solid in butanone, and pouring into methanol, but it was generally found that the extra yield of crystals obtained was too small to be worthwhile (typically another 1.0−1.5 g).

NMR data were consistent with those previously reported.[44]

2,6(7)-Dinitrotriptycene 1. Triptycene (2.54 g, 10.0 mmol) was dissolved in CH_2Cl_2 (50 mL). Cerium ammonium nitrate (11.0 g, 20.0 mmol) was added, followed by sulfuric acid (1.92 mL, 3.53 g, 36.0 mmol). The reaction was stirred at room temperature overnight under a nitrogen atmosphere, during which time it turned a deep green color. The mixture was filtered to remove the cerium salts, and the filter-cake was washed with CH_2Cl_2 until colorless. The combined organic fractions were basified with $K_2CO_{3(aq)}$ (10%, 100 mL), the organic layer was taken, and the aqueous phase was extracted with further CH_2Cl_2 (50 mL). The combined organic fractions were dried ($MgSO_4$), taken to dryness under reduced pressure, and purified by column chromatography (gradient: 2:1 to 1:1 petrol:CH_2Cl_2) to give a mixture of 2,6- and 2,7-dinitrotriptycene as a very pale yellow powder. Yield: 1.93 g (5.61 mmol, 56%).

NMR data were consistent with those previously reported.[28]

Diacetamidodinitro Triptycene 2. Ethanol (100 mL) was cooled in an ice-bath under a nitrogen atmosphere. Palladium on carbon (10 wt %, 0.34 g) was added, followed by a mixture of 2,6- and 2,7-dinitrotriptycene (**1**) (3.44 g, 10.0 mmol), and hydrazine hydrate (3.4 mL) dropwise. The reaction was heated to reflux under a nitrogen atmosphere overnight and then cooled to room temperature. A small amount of Celite was added to the reaction mixture, which was then filtered through a pad of Celite, and the filtercake was washed with ethanol (2 × 30 mL). The combined filtrates were dried under reduced pressure to give a mixture of 2,6- and 2,7-diaminotriptycene as a foamy white solid.

This mixture was suspended in acetic anhydride (100 mL) and stirred at room temperature under a nitrogen atmosphere for 30 min. *para*-Toluenesulfonic acid hydrate (4.19 g, 22.0 mmol) was added, causing all material to dissolve, followed by KNO_3 (2.12 g, 21.0 mmol). The reaction was stirred at room temperature under a nitrogen atmosphere overnight and was then poured into water (500 mL) and stirred at room temperature for an hour. The mixture was filtered to give an orange powder, which was washed with more water (3 × 100 mL). It was then dissolved in CH_2Cl_2 (150 mL), dried ($MgSO_4$), and dried under reduced pressure. Purification by column chromatography (gradient: 1−3% CH_3OH in CH_2Cl_2) gave both isomers of dinitrodiacetamidotriptycene as yellow powders. The last portion of the product that was eluted from the column was contaminated with an impurity, so this fraction was recrystallized from boiling ethanol to give pure product. Combined yield: 3.56 g (7.77 mmol, 78%).

It was possible to separate the isomers using careful column chromatography, although this was not normally conducted, and typically the mixture of isomers was reacted onward.

HRESI-MS (pos.): 481.1134, calcd. for $[C_{24}H_{18}N_4O_6{\cdot}Na]^+$ = 481.1124 (taken from the mixture of isomers).

anti-Dinitrodiacetamidotriptycene ***2***. ^{1}H NMR (300 MHz, $CDCl_3$): 10.49 (s, 2H), 8.91 (s, 2H), 8.19 (s, 2H), 7.40−7.45 (m, 2H), 7.07−7.13 (m, 2H), 5.55 (s, 2H), 2.26 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 169.3, 152.2, 142.0, 138.1, 134.3, 133.1, 126.8, 124.6, 121.0, 117.4, 52.9, 25.8 ppm. LRESI-MS (pos.): 481.4, calcd. for $[C_{24}H_{18}N_4O_6{\cdot}Na]^+$: 481.1. mp > 260 °C. R_f (19:1 CH_2Cl_2:CH_3OH): 0.44.

syn-Dinitrodiacetamidotriptycene ***2***. ^{1}H NMR (400 MHz, $CDCl_3$): 10.46 (s, 2H), 8.93 (s, 2H), 8.20 (s, 2H), 7.38−7.48 (m, 2H), 7.07−7.15 (m, 2H), 5.62 (s, 1H), 5.48 (s, 1H), 2.26 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 169.2, 151.5, 142.8, 141.3, 138.9, 134.1, 133.2, 126.8, 126.7, 125.1, 124.1, 120.5, 117.9, 54.0, 51.8, 25.8 ppm. LRESI-MS (pos.): 481.4, calcd. for $[C_{24}H_{18}N_4O_6{\cdot}Na]^+$: 481.1. mp 197−200 °C. R_f (19:1 CH_2Cl_2:CH_3OH): 0.34.

Diaminodinitrotriptycene 3. A mixture of both isomers of **2** (1.37 g, 3.00 mmol) was suspended in ethanol (30 mL). NaOH (1.2 g, 30 mmol) in water (3 mL) was added, and the yellow suspension was heated to reflux under a nitrogen atmosphere for 2 h. The suspension was dried under reduced pressure, and the resulting orange powder was suspended in water (60 mL), filtered, washed with water (3 × 5 mL) and methanol (2 × 3 mL), and dried *in vacuo* to give both isomers of diaminodinitrotriptycene as an orange powder. Yield: 0.915 g (2.44 mmol, 82%).

Typically, a mixture of isomers was used in this procedure; however, if either isomer of ***2*** *was used instead of a mixture, comparable yields were obtained, and this allowed the characterization of each isomer of* ***3****.*

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HRESI-MS (pos.): 397.0899, calcd. for $[C_{20}H_{14}N_4O_4{\cdot}Na]^+$ = 397.0913 (taken from the mixture of isomers).

anti-Dinitrodiaminotriptycene ***3***. ^{1}H NMR (300 MHz, DMSO-d_6): 7.99 (s, 2H), 7.58 (s, 4H), 7.40−7.45 (m, 2H), 7.04−7.12 (m, 4H), 5.55 (s, 2H) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): 151.5, 145.8, 142.7, 130.0, 126.6, 126.1, 123.9, 119.7, 113.7, 49.9 ppm. LRESI-MS (pos.): 397.4, calcd. for $[C_{20}H_{14}N_4O_4{\cdot}Na]^+$ = 397.1. mp > 260 °C. R_f (19:1 CH_2Cl_2:CH_3OH): 0.47.

syn-Dinitrodiaminotriptycene ***3***. ^{1}H NMR (300 MHz, DMSO-d_6): 7.93 (s, 2H), 7.38−7.55 (m, 6H), 7.00−7.11 (m, 4H), 5.57 (s, 1H), 5.54 (s, 1H) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): 150.4, 145.5, 144.1, 141.3, 131.5, 126.7, 126.3, 125.8, 124.4, 123.4, 119.0, 114.3, 51.3, 48.6 ppm. LRESI-MS (pos.): 397.4, calcd. for $[C_{20}H_{14}N_4O_4{\cdot}Na]^+$ = 397.1. mp > 260 °C. R_f (19:1 CH_2Cl_2:CH_3OH): 0.43.

Tetraaminotriptycene Tetrahydrochloride 4·4HCl. A mixture of isomers of dinitrodiaminotriptycene **3** (0.936 g, 2.5 mmol) was suspended in ethanol (35 mL) and conc. $HCl_{(aq)}$ (15 mL). $SnCl_2{\cdot}2H_2O$ (11 g, 50 mmol) was added, and the orange suspension was heated to reflux overnight under nitrogen. During this time, everything dissolved to give a pale yellow solution. This was cooled to room temperature and then taken to dryness under reduced pressure. The resulting white solid was suspended in conc. $HCl_{(aq)}$ (20 mL) and heated to reflux for 10 min. The mixture was cooled to room temperature and then filtered to give a white powder, which was washed with further conc. $HCl_{(aq)}$ (4 × 10 mL) and then dried *in vacuo*. This solid was recrystallized from boiling EtOH (100 mL) to give fluffy off-white crystals, which were isolated by filtration, washed with cold EtOH (3 × 10 mL), and dried thoroughly *in vacuo* at 65 °C to give **4·4HCl**. Yield: 0.645 g (1.41 mmol, 56%).

Note: it is difficult to remove all trace of ethanol from this compound. On thorough drying in vacuo at 65 °C, essentially all the ethanol can be removed, but during this process, the white crystalline solid turns a gray color. Despite this color change, the ^{1}H and ^{13}C NMR spectra remain unchanged (apart from intensity of the EtOH resonances decreasing to almost nothing). No further color change (or change in the NMR spectrum) is observed on storing at ambient temperature and atmosphere for several months.

^{1}H NMR (300 MHz, CD_3OD): 7.36−7.40 (m, 2H,), 7.27 (s, 4H), 6.98−7.01 (m, 2H), 5.47 (s, 2H) ppm. ^{13}C NMR (75 MHz, CD_3OD): 145.7, 144.0, 126.6, 126.2, 124.6, 118.3, 53.4 ppm. HRESI-MS (pos.): 315.1606, calcd. for $[C_{20}H_{18}N_4{\cdot}H]^+$ = 315.1610. mp > 260 °C.

Triptycene Bis-imidazole 5. Tetraaminotriptycene·4HCl (0.138 g, 0.300 mmol) was dissolved in methanol (5 mL). Trimethylorthoformate (0.072 mL, 0.070 g, 0.66 mmol) in methanol (1 mL) was added, and the pale yellow solution was heated to reflux under a nitrogen atmosphere overnight, during which time a very pale yellow solid precipitated. The reaction mixture was cooled to room temperature and triethylamine (0.21 mL, 0.15 g, 1.5 mmol) was added, and the suspension was stirred for 10 min. It was filtered to give a white solid, which was washed with methanol (4 × 2 mL) and dried thoroughly to give 0.052 g (52%) of **5**. The filtrate was taken to dryness under reduced pressure, and the pale yellow solid was taken up in 3:1 methanol:dichloromethane (8 mL). The volume of the solution was reduced to 4 mL by boiling, and then the solution was allowed to cool to room temperature. This gave a white solid, which was isolated by filtration, washed with cold methanol (2 × 2 mL), and dried thoroughly to give an additional 0.020 g (20%) of **5** as a white powder. Combined yield: 0.072 g (0.22 mmol, 72%).

^{1}H NMR (300 MHz, DMSO-d_6): 12.28 (s, 2H), 8.08 (s, 2H), 7.62 (br. s, 4H), 7.41−7.44 (m, 2H), 6.96−6.99 (m, 2H), 5.69 (s, 2H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6): 146.1, 141.7, 139.9, 135.1, 124.9, 123.3, 110.5, 52.8 ppm. HRESI-MS (pos.): 335.1292, calcd. for $[C_{22}H_{14}N_4{\cdot}H]^+$ = 335.1297. mp > 260 °C.

Hexanitrotriptycene 7.[17] ***Caution!*** *While we did not experience any problems in the course of this work, the nitric/sulfuric acid mixture used in this reaction is extremely corrosive and oxidizing. Hexanitrotriptycene is potentially explosive.*

Fuming nitric acid (90% aq., 24 mL) was cooled in an ice-bath. Under a nitrogen atmosphere, sulfuric acid (6 mL) was cautiously added dropwise, followed by triptycene (2.54 g, 10.0 mmol) portionwise. The reaction was heated to 85 °C while open to the air overnight, during which time a white powder precipitated from the orange-brown solution. The mixture was cooled to room temperature, cautiously poured into water (500 mL), and stirred for 5 min. The white suspension was filtered, washed with water (3 × 50 mL), and dried *in vacuo*. Recrystallization from boiling acetone (500 mL) gave colorless crystals, which were isolated by filtration, washed with cold acetone (3 × 20 mL), and dried *in vacuo*. Yield: 1.48 g (28%). The filtrate was reduced in volume to 250 mL and cooled to −20 °C to yield additional colorless crystals, which were isolated in the same manner. Yield: 0.743 g (14%). Total yield of **7**: 2.22 g (4.23 mmol, 42%).

NMR data were consistent with the literature.[17] *The product is approximately 90% pure at this point (it contains small traces of pentanitrotriptycene and 1,3,7,8,14,15-hexanitrotriptycene; see Figure S6).*

Methoxyphenyl-Substituted Tetraamine 8. Hexaaminotriptycene·6HCl·8H_2O (1.4 g, 2.0 mmol) was suspended in methanol (100 mL) and sonicated for 20 min to thoroughly disperse the insoluble compound. The resulting milky white suspension was heated to reflux under a nitrogen atmosphere, and a solution of anisil (0.270 g, 1.00 mmol) and triethylamine (3.3 mL, 2.4 g, 24 mmol) in chloroform (100 mL) was added in one portion. The resulting clear yellow-orange solution was heated to reflux under a nitrogen atmosphere overnight. It was cooled to room temperature and taken to dryness under reduced pressure to give a brown solid. This was suspended in dichloromethane (100 mL), and filtered through a short pad of Celite, washing the solid with further dichloromethane (2 × 50 mL). The resulting clear yellow filtrate was washed with $K_2CO_{3(aq)}$ (10%, 2 × 100 mL), dried ($MgSO_4$), and taken to dryness under reduced pressure. Purification by column chromatography (gradient: 5−10% methanol in dichloromethane gave **8** as an orange powder, as well as the doubly reacted diamine **9** as an orange powder. Yield of **8**: 0.334 g (0.578 mmol, 58%). Yield of **9**: 0.079 g (0.097 mmol, 19%).

^{1}H NMR (300 MHz, $CDCl_3$): 7.88 (s, 2H), 7.39 (d, J = 8.7 Hz, 4H), 6.79−6.85 (m, 8H), 5.24 (s, 2H), 3.81 (s, 6H), 3.25 (br. s, 8H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): 160.0, 151.9, 147.7, 140.2, 136.9, 132.2, 131.9, 131.3, 121.5, 113.8, 113.2, 55.4, 52.5 ppm. HRESI-MS (pos.): 579.2513, calcd. for $[C_{36}H_{30}N_6O_2{\cdot}H]^+$ = 579.2508. mp > 260 °C. R_f (9:1 CH_2Cl_2:CH_3OH): 0.30.

Methoxyphenyl-Substituted Diamine 9. Hexaaminotriptycene·6HCl·8H_2O (0.141 g, 0.200 mmol) was suspended in methanol (10 mL) and sonicated for 20 min to thoroughly disperse the insoluble compound. The resulting milky white suspension was heated to reflux under a nitrogen atmosphere, and a solution of dimethoxybenzil (0.108 g, 0.400 mmol) and triethylamine (0.33 mL, 0.24 g, 2.4 mmol) in chloroform (10 mL) was added in one portion. The resulting clear yellow-orange solution was heated to reflux overnight under nitrogen, and then taken to dryness under reduced pressure to give a golden solid. This was dissolved in CH_2Cl_2 (20 mL), washed with $K_2CO_{3(aq)}$ (10%, 2 × 20 mL), dried ($MgSO_4$), and taken to dryness under reduced pressure. Purification by column chromatography (gradient: 2−7% methanol in dichloromethane gave diamine **9** as a yellow-orange powder. Yield: (0.078 g, 0.096 mmol, 48%). The triply reacted byproduct hexakis(methoxyphenyl)tris(pyrazinyl)triptycene[17] was also obtained (yield: 0.040 g, 0.038 mmol, 29%), as well as small quantities of tetraamine **8**.

^{1}H NMR (400 MHz, $CDCl_3$): 8.03 (s, 4H), 7.41 (d, J = 8.4 Hz, 8H), 6.92 (s, 2H), 6.83 (d, J = 8.4 Hz, 8H), 5.62 (s, 2H), 3.80 (s, 12H), 3.36 (br. s, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 160.1, 152.4, 145.6, 140.2, 135.2, 132.5, 131.9, 131.3, 122.7, 113.8, 113.5, 55.4, 52.8 ppm. HRESI-MS (pos.): 813.3190, calcd. for $[C_{52}H_{40}N_6O_4{\cdot}H]^+$ = 813.3189. mp > 260 °C. R_f (19:1 CH_2Cl_2:CH_3OH): 0.30.

Hexyloxyphenyl-Substituted Tetraamine 10. Hexaaminotriptycene·6HCl·8H_2O (0.71 g, 1.0 mmol) was suspended in methanol (50 mL) and sonicated for 20 min to thoroughly disperse the insoluble compound. The resulting milky white suspension was heated to reflux under a nitrogen atmosphere, and a solution of bis(hexyloxy)benzil (0.135 g, 0.500 mmol) and triethylamine (1.7 mL, 1.2 g, 12 mmol) in chloroform (50 mL) was added in one portion. The resulting clear yellow-orange solution was heated to reflux under a nitrogen

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J. Org. Chem. 2015, 80, 8390−8397

atmosphere overnight; then it was cooled to room temperature and dried under reduced pressure to give a brown solid. This solid was suspended in dichloromethane (50 mL) and filtered through a short pad of Celite, washing the solid with dichloromethane (2 × 25 mL). The resulting clear yellow filtrate was washed with $K_2CO_{3(aq)}$ (10%, 2 × 50 mL), dried ($MgSO_4$), and taken to dryness under reduced pressure. Purification by column chromatography (gradient: 4−7% methanol in dichloromethane) gave **10** as an orange powder. Yield: 0.189 g (0.263 mmol, 53%).

^{1}H NMR (400 MHz, $CDCl_3$): 7.87 (s, 2H), 7.37 (d, J = 8.7 Hz, 4H), 6.79−6.84 (m, 8H), 5.23 (s, 2H), 3.95 (t, J = 6.7 Hz, 4H), 3.26 (br. s, 8H), 1.77 (app. qn, J = 6.7 Hz, 4H), 1.29−1.50 (m, 12H), 0.91 (t, J = 6.7 Hz, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): 159.5, 152.0, 147.6, 140.2, 136.9, 131.95, 131.90, 131.2, 121.5, 114.3, 113.2, 68.2, 52.5, 31.7, 29.3, 25.8, 22.7, 14.2 ppm. HRESI-MS (pos.): 739.3755, calcd. for $[C_{34}H_{52}N_8O_9{\cdot}Na]^+$ = 739.3755. mp 178−180 °C. R_f (9:1 CH_2Cl_2:CH_3OH): 0.37.

Hexyl-Substituted Tetraamine 11. Hexaaminotriptycene·6HCl·$8H_2O$ (0.71 g, 1.0 mmol) was suspended in methanol (50 mL) and sonicated for 20 min to thoroughly disperse the insoluble compound. The resulting milky white suspension was heated to reflux under a nitrogen atmosphere, and a solution of 7,8-tetradecanedione (0.113 g, 0.500 mmol) and triethylamine (1.7 mL, 1.2 g, 12 mmol) in chloroform (50 mL) was added in one portion. The resulting clear yellow-orange solution was heated to reflux under a nitrogen atmosphere overnight. It was cooled to room temperature and dried under reduced pressure to give a brown solid. The solid was suspended in dichloromethane (50 mL) and filtered through a short pad of Celite, washing the solid with dichloromethane (2 × 25 mL). The resulting clear yellow filtrate was washed with $K_2CO_{3(aq)}$ (10%, 2 × 50 mL), dried ($MgSO_4$), and taken to dryness under reduced pressure. Purification by column chromatography (gradient: 7−10% methanol in dichloromethane) gave **11** as a yellow-orange powder. Yield: 0.164 g (0.307 mmol, 61%). ^{1}H NMR (300 MHz, $CDCl_3$): 7.75 (s, 2H), 6.80 (s, 4H), 5.20 (s, 2H), 3.17 (br. s, 8H), 2.91 (t, J = 6.8 Hz, 4H), 1.66−1.76 (m, 4H), 1.23−1.46 (m, 12H), 0.88 (t, J = 6.8 Hz, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): 155.4, 146.7, 139.9, 137.1, 131.8, 121.1, 113.2, 52.5, 35.4, 31.9, 29.5, 29.3, 22.7, 14.2 ppm. HREI-MS: 534.3466, calcd. for $[C_{34}H_{42}N_6]^+$ = 534.3471. mp 183−185 °C. R_f (9:1 CH_2Cl_2:CH_3OH): 0.33.

Methoxyphenyl-Substituted Bis(imidazole) 12. Methoxyphenyl-substituted tetraamine **8** (0.058 g, 0.10 mmol) and NH_4Cl (0.11 g, 2.0 mmol) were placed in a flask. Ethanol (10 mL) was added, and the yellow suspension was heated to reflux under a nitrogen atmosphere. Trimethyl orthoformate (0.055 mL, 0.053 g, 0.50 mmol) was then added, and the reaction mixture was heated to reflux under a nitrogen atmosphere for 48 h. Drying under reduced pressure gave a brown powder, which was suspended in saturated $NaHCO_{3(aq)}$, sonicated briefly, and then filtered. The pale brown powder was washed with saturated $NaHCO_{3(aq)}$ (2 × 5 mL) and water (4 × 5 mL); then it was dissolved using 2:1 CH_2Cl_2:CH_3OH to give a yellow solution. Upon drying under reduced pressure, compound **12** was obtained as a pale brown powder. Yield: 0.048 g (0.080 mmol, 80%).

^{1}H NMR (400 MHz, 1:1 $CDCl_3$:CD_3OD): 8.04 (s, 2H), 7.99 (s, 2H), 7.42 (d, J = 7.4 Hz, 4H), 6.83 (d, J = 7.4 Hz, 4H), 5.83 (s, 2H), 3.78 (s, 6H) ppm.^{13}C NMR (100 MHz, 1:1 $CDCl_3$:CD_3OD): 160.9, 153.2, 148.0, 141.6, 140.4, 139.8, 135.91, 135.85, 131.7, 122.3, 114.2, 111.5, 55.6, 54.4 ppm. HRESI-MS (pos.): 599.2190, calcd. for $[C_{38}H_{26}N_6O_2{\cdot}H]^+$ = 599.2195. mp > 260 °C.

Hexyloxyphenyl-Substituted Bis(imidazole) 13. Hexyloxyphenyl-substituted tetraamine **10** (0.072 g, 0.10 mmol) and NH_4Cl (0.11 g, 2.0 mmol) were placed in a flask. Ethanol (10 mL) and trimethyl orthoformate (0.055 mL, 0.053 g, 0.50 mmol) were added, and the reaction mixture was heated to reflux under a nitrogen atmosphere for 48 h. Drying under reduced pressure gave a yellow powder. This was suspended in saturated $NaHCO_{3(aq)}$, sonicated briefly, and then filtered to give a yellow powder, which was washed with saturated $NaHCO_{3(aq)}$ (2 × 5 mL), and water (4 × 5 mL). The solid was dissolved using 2:1 CH_2Cl_2:CH_3OH to give a yellow solution, which was taken to dryness under reduced pressure to give **13** as a pale yellow powder. Yield: 0.077 g (0.096 mmol, 96%).

^{1}H NMR (400 MHz, 1:1 $CDCl_3$:CD_3OD): 8.10 (s, 2H), 8.05 (s, 2H), 7.75 (s, 4H), 7.31 (d, J = 8.6 Hz, 4H), 6.82 (d, J = 8.6 Hz, 4H), 5.85 (s, 2H), 3.95 (t, J = 6.4 Hz, 4H), 1.71−1.80 (m, 4H), 1.23−1.50 (m, 12H), 0.88 (t, J = 6.6 Hz, 6H) ppm. ^{13}C NMR (100 MHz, 1:1 $CDCl_3$:CD_3OD): 160.4, 153.4, 147.7, 141.4, 140.4, 140.1, 135.3, 131.7, 131.5, 122.4, 114.8, 111.4, 68.6, 54.4, 32.1, 29.7, 26.2, 23.1, 14.2 ppm. HRESI-MS (pos.): 739.3765, calcd. for $[C_{48}H_{46}N_6O_2{\cdot}H]^+$ = 739.3761. mp > 260 °C.

Hexyl-Substituted Bis(imidazole) 14. Hexyl-substituted tetraamine **11** (0.053 g, 0.10 mmol) and NH_4Cl (0.11 g, 2.0 mmol) were placed in a flask. Ethanol (10 mL) and trimethyl orthoformate (0.055 mL, 0.053 g, 0.50 mmol) were added, and the reaction mixture was heated to reflux under a nitrogen atmosphere for 48 h. Drying the solution under reduced pressure afforded a brown powder that was suspended in saturated $NaHCO_{3(aq)}$, sonicated briefly, and then filtered to give a pale brown powder. The solid was washed with saturated $NaHCO_{3(aq)}$ (2 × 5 mL) and water (4 × 5 mL); then it was dissolved using 2:1 CH_2Cl_2:CH_3OH to give a yellow solution, which was taken to dryness under reduced pressure to give **14** as a pale brown powder. Yield: 0.052 g (0.093 mmol, 93%).

^{1}H NMR (400 MHz, 1:1 $CDCl_3$:CD_3OD): 7.97 (s, 2H), 7.93 (s, 2H), 7.70 (s, 4H), 5.79 (s, 2H), 2.91 (t, J = 7.8 Hz, 4H), 1.65−1.72, (m, 4H), 1.23−1.45 (m, 12H), 0.84 (t, J = 6.7 Hz, 6H) ppm. ^{13}C NMR (100 MHz, 1:1 $CDCl_3$:CD_3OD): 156.6, 147.2, 141.6, 140.1, 139.9, 135.9, 121.8, 111.4, 54.4, 35.6, 32.1, 29.9, 29.8, 23.0, 14.2 ppm. HRESI-MS (pos.): 555.3234, calcd. for $[C_{36}H_{38}N_6{\cdot}H]^+$ = 555.3236. mp > 260 °C.

Triptycene Bis(dimethylpyrazine) 15. Methoxyphenyl-substituted tetraamine **8** (0.029 g, 0.050 mmol) and butadione (0.018 mL, 0.017 g, 0.20 mmol) were placed in a round-bottom flask. A 1:1 v/v mixture of $CHCl_3$ and CH_3OH (10 mL) was added, and the resulting clear orange solution was heated to reflux under a nitrogen atmosphere overnight, during which time the solution became yellow. The mixture was cooled to room temperature, taken to dryness under reduced pressure, and dried thoroughly to give **15** as a pale yellow powder. Yield: 0.029 g (0.043 mmol, 85%).

^{1}H NMR (400 MHz, $CDCl_3$): 8.18 (s, 2H), 8.07 (s, 4H), 7.41 (d, J = 8.7 Hz, 4H), 6.83 (d, J = 8.7 Hz, 4H), 6.00 (s, 2H), 3.81 (s, 6H), 2.68 (s, 12H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 160.2, 153.3, 152.9, 143.9, 143.3, 140.2, 140.1, 131.7, 131.3, 123.7, 123.1, 113.9, 55.4, 53.2, 23.0 ppm. HRESI-MS (pos.): 679.2841, calcd. for $[C_{44}H_{34}N_6O_2{\cdot}H]^+$ = 679.2821. mp > 260 °C. R_f (19:1 CH_2Cl_2:CH_3OH): 0.49.

Triptycene Bis(triptycene) 16. Methoxyphenyl-substituted tetraamine **8** (0.029 g, 0.050 mmol) and triptycene quinone (0.028 g, 0.10 mmol) were placed in a round-bottom flask. A 1:1 v/v mixture of $CHCl_3$ and CH_3OH (10 mL) was added, and the resulting clear orange solution was heated to reflux under a nitrogen atmosphere overnight. The mixture was cooled to room temperature, taken to dryness under reduced pressure, and purified by preparative TLC (19:1 CH_2Cl_2:CH_3OH) to give **16** as a pale yellow powder. Yield: 0.045 g (0.042 mmol, 84%).

^{1}H NMR (300 MHz, $CDCl_3$): 8.26 (s, 4H), 8.23 (s, 2H), 8.04 (s, 4H), 7.44−7.49 (m, 8H), 7.39 (d, J = 8.7 Hz, 4H), 7.04−7.10 (m, 8H) 6.82 (d, J = 8.7 Hz, 4H), 6.07 (s, 2H), 5.63 (s, 4H), 3.80 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 160.3, 153.1, 146.9, 143.5, 143.30, 143.28, 142.7, 142.6, 142.2, 140.5, 131.6, 131.3, 126.4, 124.3, 124.2, 123.7, 122.2, 113.9, 55.4, 53.6, 53.1 ppm. HRESI-MS (pos.): 1075.3730, calcd. for $[C_{76}H_{46}N_6O_2{\cdot}H]^+$ = 1075.3761. mp > 260 °C. R_f (19:1 CH_2Cl_2:CH_3OH): 0.57.

Triptycene Bis(di-*tert*-butylpyrene) 17. Methoxyphenyl-substituted tetraamine **8** (0.029 g, 0.050 mmol) and di-^{t}Bu-pyrene dione (0.034 g, 0.10 mmol) were placed in a round-bottom flask. A 1:1 v/v mixture of $CHCl_3$ and CH_3OH (10 mL) was added, and the resulting clear orange solution was heated to reflux under a nitrogen atmosphere overnight. During this time, a pale yellow powder precipitated from the reaction mixture. The mixture was cooled to room temperature, taken to dryness under reduced pressure, and purified by preparative

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J. Org. Chem. 2015, 80, 8390−8397

TLC (2:3 petrol:CH_2Cl_2) to give **17** as a yellow powder. Yield: 0.046 g (0.039 mmol, 77%).

^{1}H NMR (300 MHz, $CDCl_3$): 9.64 (d, ^4J = 1.7 Hz, 4H), 8.59 (s, 4H), 8.32 (s, 2H), 8.25 (d, J = 1.7 Hz, 4H), 7.97 (s, 4H), 7.43 (d, J = 8.7 Hz, 4H), 6.85 (d, J = 8.7 Hz, 4H), 6.27 (s, 2H), 3.82 (s, 6H), 1.67 (s, 36 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): 160.2, 153.0, 149.8, 143.9, 143.73, 143.67, 141.6, 140.6, 131.8, 131.3, 131.2, 129.1, 127.4, 125.8, 124.3, 124.2, 123.9, 121.5, 113.9, 55.4, 53.6, 35.7, 32.0 ppm. HRESI-MS (pos.): 1195.5663, calcd. for $[C_{84}H_{70}N_6O_2{\cdot}H]^+$ = 1195.5639. mp > 260 °C. R_f (CH_2Cl_2): 0.49. UV−vis (CH_2Cl_2), λ_{max} (log ε): 290 (5.2), 316 (4.7), 331 (4.7), 356 (4.7), 425 (4.5), 452 (4.6) nm.

Triptycene Bis(phenanthroline) 18. Methoxyphenyl-substituted tetraamine **8** (0.058 g, 0.10 mmol) and phenanthroline dione (0.042 g, 0.20 mmol) were placed in a round-bottom flask. A 1:1 v/v mixture of $CHCl_3$ and CH_3OHc(10 mL) was added, and the resulting clear orange solution was heated to reflux under a nitrogen atmosphere overnight, during which time the reaction mixture became noticeably lighter in color. The reaction mixture was taken to dryness under reduced pressure, and the resulting pale yellow was dissolved in CH_2Cl_2 (3 mL) and added to CH_3OH (12 mL) to precipitate **18** as a fine pale yellow powder. The product was isolated by centrifugation and dried *in vacuo*. Yield: 0.079 g (0.085 mmol, 85%).

^{1}H NMR (300 MHz, $CDCl_3$): 9.41 (d, J = 7.8 Hz, 4H), 9.14−9.16 (m, 4H), 8.39−8.42 (m, 6H), 7.61−7.64 (m, 4H), 7.48 (d, J = 8.4 Hz, 4H), 6.86 (d, J = 8.4 Hz, 4H), 6.25 (s, 2H), 3.82 (s, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): 160.4, 153.4, 152.3, 147.6, 144.4, 142.9, 141.8, 140.7, 140.5, 133.8, 131.5, 131.4, 127.3, 124.4, 124.3, 124.2, 114.0, 55.5, 53.3 ppm. HRESI-MS (pos.): 927.2907, calcd. for $[C_{60}H_{34}N_{10}O_2{\cdot}H]^+$ = 927.2944. . mp > 260 °C.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01221.

Details of instrumentation, optimization of dinitration of triptycene, NMR spectra of new compounds, thermal ellipsoid plot of crystal structure of **12**, optical and fluorescence spectra of **17** (PDF)

Full crystallographic data for **12** (CIF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Chong, J. H.; MacLachlan, M. J. *Chem. Soc. Rev.* **2009**, *38*, 3301−3315.

(2) Han, Y.; Meng, Z.; Ma, Y.-X.; Chen, C.-F. *Acc. Chem. Res.* **2014**, *47*, 2026−2040.

(3) Chen, C.-F. *Chem. Commun.* **2011**, *47*, 1674−1688.

(4) Ma, Y.-X.; Meng, Z.; Chen, C.-F. *Synlett* **2015**, *26*, 6−30.

(5) Yang, J.-S.; Swager, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 5321−5322.

(6) Long, T. M.; Swager, T. M. *J. Am. Chem. Soc.* **2003**, *125*, 14113−14119.

(7) VanVeller, B.; Robinson, D.; Swager, T. M. *Angew. Chem., Int. Ed.* **2012**, *51*, 1182−1186.

(8) Kelly, T. R.; De Silva, H.; Silva, R. A. *Nature* **1999**, *401*, 150−152.

(9) Nikitin, K.; Müller-Bunz, H.; Ortin, Y.; Muldoon, J.; McGlinchey, M. J. *J. Am. Chem. Soc.* **2010**, *132*, 17617−17622.

(10) Zhu, X.-Z.; Chen, C.-F. *J. Am. Chem. Soc.* **2005**, *127*, 13158−13159.

(11) Meng, Z.; Xiang, J.-F.; Chen, C.-F. *Chem. Sci.* **2014**, *5*, 1520−1525.

(12) Zhang, G.; Presly, O.; White, F.; Oppel, I. M.; Mastalerz, M. *Angew. Chem., Int. Ed.* **2014**, *53*, 5126−5120.

(13) Mastalerz, M.; Schneider, M. W.; Oppel, I. M.; Presly, O. *Angew. Chem., Int. Ed.* **2011**, *50*, 1046−1051.

(14) Zhang, G.; Mastalerz, M. *Chem. Soc. Rev.* **2014**, *43*, 1934−1947 and references therein.

(15) Zhang, G.; Presly, O.; White, F.; Oppel, I. M.; Mastalerz, M. *Angew. Chem., Int. Ed.* **2014**, *53*, 1516−1520.

(16) Chong, J. H.; MacLachlan, M. J. *Inorg. Chem.* **2006**, *45*, 1442−1444.

(17) Mastalerz, M.; Sieste, S.; Cenić, M.; Oppel, I. M. *J. Org. Chem.* **2011**, *76*, 6389−6393.

(18) Mastalerz, M.; Oppel, I. M. *Angew. Chem., Int. Ed.* **2012**, *51*, 5252−5255.

(19) Rabbani, M. G.; Reich, T. E.; Kassab, R. M.; Jackson, K. T.; El-Kaderi, H. M. *Chem. Commun.* **2012**, *48*, 1141−1143.

(20) Sekizkardes, A. K.; Altarawneh, S.; Kahveci, Z.; İslamoğlu, T.; El-Kaderi, H. M. *Macromolecules* **2014**, *47*, 8328−8334.

(21) Sekizkardes, A. K.; İslamoğlu, T.; Kahveci, Z.; El-Kaderi, H. M. *J. Mater. Chem. A* **2014**, *2*, 12492−12500.

(22) Chong, J. H.; Ardakani, S. J.; Smith, K. J.; MacLachlan, M. J. *Chem. - Eur. J.* **2009**, *15*, 11824−11828.

(23) Anselmo, D.; Salassa, G.; Escudero-Adán, E. C.; Martin, E.; Kleij, A. W. *Dalton Trans.* **2013**, *42*, 7962−7970.

(24) Li, Y.; Cao, R.; Lippard, S. J. *Org. Lett.* **2011**, *13*, 5052−5055.

(25) Chong, J. H.; MacLachlan, M. J. *J. Org. Chem.* **2007**, *72*, 8683−8690.

(26) Roy, X.; Chong, J. H.; Patrick, B. O.; MacLachlan, M. J. *Cryst. Growth Des.* **2011**, *11*, 4551−4558.

(27) Klanderman, B. H.; Perkins, W. C. *J. Org. Chem.* **1969**, *34*, 630−633.

(28) Chen, Z.; Swager, T. M. *Macromolecules* **2008**, *41*, 6880−6885.

(29) Sydlik, S. A.; Chen, Z.; Swager, T. M. *Macromolecules* **2011**, *44*, 976−980.

(30) Mellor, J. M.; Mittoo, S.; Parkes, R.; Millar, R. W. *Tetrahedron* **2000**, *56*, 8019−8024.

(31) Mastalerz et al. report **6**·6HCl analyzing as the heptahydrate (ref 17).

(32) CD_2Cl_2 was used instead of $CDCl_3$, as the tetraamines appear to be sensitive to a decomposition product of $CDCl_3$. While satisfactory NMR spectra could be obtained using $CDCl_3$, using older $CDCl_3$, or standing in $CDCl_3$ for extended periods of time gave extremely broad spectra. Adding NEt_3 to the sample restored a sharp spectrum, but with the appearance of several major decomposition products. When **8** was dissolved in CD_2Cl_2 containing TFA for 2 h, and then neutralized with NEt_3, an unchanged ^{1}H NMR spectrum was obtained, suggesting that **8** is not sensitive to acid, but rather to a decomposition product of $CDCl_3$.

(33) (a) Single-crystal X-ray data were collected using Mo Kα radiation (λ = 0.71073 Å) at 90 K. Raw frame data (including data reduction, interframe scaling, unit cell refinement, and absorption corrections) for all structures were processed using: *APEX2*; Bruker AXS Inc.: Madison, WI, 2007. (b) Structures were solved using SUPERFLIP: Palatinus, L.; Chapuis, G. *J. Appl. Crystallogr.* **2007**, *40*, 786−790. (c) Structures were refined using full-matrix least-squares on F^2 within the CRYSTALS suite: Betteridge, P. W.; Carruthers, J. R.; Cooper, R. I.; Prout, K.; Watkin, D. J. *J. Appl. Crystallogr.* **2003**, *36*, 1487. Full crystallographic data in CIF format are provided as Supporting Information [CCDC Number: 1403765].

(34) Alvarez, S. *Dalton Trans.* **2013**, *42*, 8617−8636.

(35) The coordination chemistry of molecules derived from **8** will be reported in due course.

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(36) Corey, E. J.; Lee, D.-H.; Sarshar, S. *Tetrahedron: Asymmetry* **1995**, *6*, 3−6.
(37) Bui, T.-T.; Garreau-de Bonneval, B.; Moineau-Chane Ching, K. I. *New J. Chem.* **2010**, *34*, 337−347.
(38) Babudri, F.; Fiandanese, V.; Marchese, G.; Punzi, A. *Tetrahedron Lett.* **1995**, *36*, 7305−7308.
(39) Hu, J.; Zhang, D.; Harris, F. W. *J. Org. Chem.* **2005**, *70*, 707−708.
(40) Zhao, J.-M.; Lu, H.-Y.; Cao, J.; Jiang, Y.; Chen, C.-F. *Tetrahedron Lett.* **2009**, *50*, 219−222.
(41) Peng, X.-X.; Lu, H.-Y.; Han, T.; Chen, C.-F. *Org. Lett.* **2007**, *9*, 895−898.
(42) Zhao, L.; Li, Z.; Wirth, T. *Chem. Lett.* **2010**, *39*, 658−667.
(43) Friedman, L.; Logullo, F. M. *J. Am. Chem. Soc.* **1963**, *85*, 1549.
(44) Kitamura, T.; Yamane, M.; Inoue, K.; Todaka, M.; Fukatsu, N.; Meng, Z.; Fujiwara, Y. *J. Am. Chem. Soc.* **1999**, *121*, 11674−11679.

DOI: 10.1021/acs.joc.5b01221
J. Org. Chem. 2015, 80, 8390−8397