

One-Pot Condensation of 2- and 2,5-Halo-Substituted Benzophenones for the Synthesis of Halo-Substituted 9,10-Diphenylanthracenes

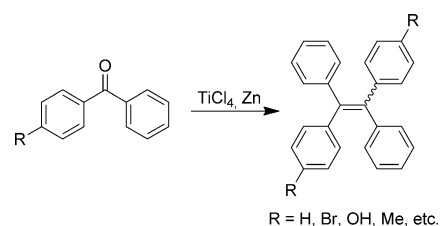
Miaomiao Xue,^[a] Liyuan Ding,^[a] Liya Lin,^[a] Yahong Lu,^[a] Bairong He,^[a] Yuan Deng,^[c] Yanju Guo,^[a] Yuning Hong,^[b] Jacky W. Y. Lam,^[b] Huayu Qiu,^[a] Zujin Zhao,^{*[a]} and Ben Zhong Tang^{*[b]}

Anthracene is one of the most important aromatic fluorophores and has been the subject of numerous investigations since Pope et al.^[1] first reported its electroluminescence. Currently, anthracene is widely used as a building block for conjugated small molecules, oligomers, dendrimers, and polymers for applications in organic light-emitting diodes (OLEDs),^[2] field-effect transistors,^[3] solar cells,^[4] chemosensors,^[5] and so on. Anthracene is generally obtained by separation from coal tar and undergoes multistep chemical modifications to afford desired intermediates, such as 9-bromoanthracene, 9,10-dibromoanthracene, 2,6-dimethyl-9,10-dibromoanthracene, anthracene-9,10-dione and 2,6-dibromoanthracene-9,10-dione, for the synthesis of anthracene-based linear and cross-conjugated materials.^[6]

Among many anthracene derivatives, 9,10-diphenylanthracene (DPA) is a remarkable chromophore with excellent blue fluorescence in dilute solution. The drawback of DPA is its high tendency towards crystallization, which decreases the fluorescence efficiency and undermines the performance of OLEDs. Chemically grafting groups with electron-donating or electron-accepting ability as well as bulky volume onto DPA frameworks is a popular method to obtain the desired optoelectronic properties and to control the stacking pattern of the materials in the solid state.^[2a,7,8] However, the synthetic methods for making DPA derivatives, particularly the construction of an anthracene frame-

work with halogen atoms at specific positions, are quite limited and involve complicated multistep procedures.^[6]

In our previous works, we were interested in exploring efficient luminescent materials with intriguing aggregation-induced emission (AIE) characteristic.^[9] Tetraphenylethene (TPE) is an archetypal luminogen with an outstanding AIE effect.^[10] We have efficiently prepared TPE and various TPE derivatives, such as 1,2-bis(4-bromophenyl)-1,2-diphenylethene and 1,2-diphenyl-1,2-dip-tolyethene, from benzophenone and 4-substituted benzophenones by the McMurry reaction,^[11] which is a classic method for constructing double bonds (Scheme 1). However, TPE derivatives with



Scheme 1. Syntheses of TPE and its derivatives as “normal” products of the McMurry reaction.

halogen atoms at the C2 position of the phenyl rings (**2a** and **2b** in Scheme 2 and **4a–4c** in Scheme 3 below) are not obtained when 2-halogenated or 2,5-dihalogenated benzophenones are used as starting materials. Interestingly, unexpected products with strong blue fluorescence are obtained instead. Herein, we report the synthesis and characterization of these blue chromophores. The mechanism for the formation of such “abnormal” products from McMurry reactions is discussed.

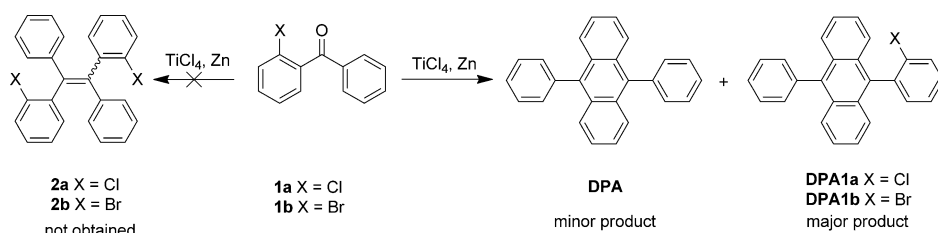
The treatment of 2-chlorobenzophenone (**1a**) with TiCl₄ and excess zinc dust gives monochlorinated DPA derivative **DPA1a** (35% yield) and DPA (Figure S1 in the Supporting Information). When 2-bromobenzophenone is used as a substrate in the reaction, similar products, monobrominated DPA derivative **DPA1b** (28% yield) and the byproduct DPA, are also obtained (Scheme 2). The yield of DPA in both reactions is less than 10%. To verify whether the reactions are feasible for more complicated substrates, three 2,5-dihalo-substituted benzophenones were prepared from commercially available 2-aminobenzophenone as described

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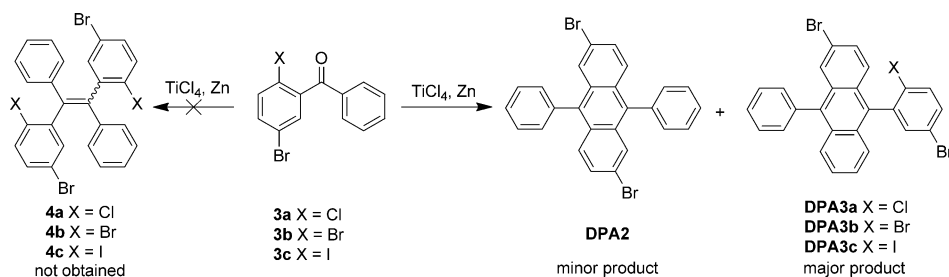
Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ajoc.201200111>.



Scheme 2. Syntheses of 9,10-diphenylanthracenes and monohalogenated 9,10-diphenylanthracenes as “abnormal” products of the McMurry reaction.

in the Supporting Information. The treatment of 2,5-dibromobenzophenone (**3b**) with TiCl_4 and excess zinc dust generates dibrominated **DPA2** and tribrominated **DPA3b** in isolated yields of 8%, and 55%, respectively. Similar products **DPA3a** and **DPA3c** were also obtained in 52 and 45% yields, respectively, with a small amount of **DPA2** when 5-bromo-2-chlorobenzophenone (**3a**) and 5-bromo-2-iodobenzophenone (**3c**) were used as starting materials for the reactions (Scheme 3). The yields of these DPA derivatives are somewhat low, probably because the reaction conditions are not fully optimized. These products have rarely been reported from McMurry reactions in the literature. Only one similar case of the formation of an alkylated anthracene was found by Stryker and co-workers in the synthesis of sterically hindered *ortho*-substituted tetraphenyl-ethenes.^[12]

The chemical structures of **DPA1a**, **DPA1b**, **DPA2**, and **DPA3a–DPA3c** were characterized by standard spectroscopic methods with satisfactory results (see the Experimental Section in the Supporting Information). Single crystals were grown from THF/ethanol mixtures and analyzed by X-ray diffraction crystallography. Figure 1 shows the crystal structures of the products. The results confirm that these new molecules have DPA frameworks. There is one halogen atom at the *ortho* position of the phenyl rings of **DPA1a** and **DPA1b**. There are two bromine atoms attached at the C2 and C6 positions of the anthracene ring in **DPA2**. In the case of **DPA3a–DPA3c**, one bromine atom is located at the C2 position of the anthracene ring and the 5-bromo-2-chloro/bromo/iodophenyl groups derived from the 2,5-halo-substituted benzophenones are linked at the C10 position of the anthracene ring.



Scheme 3. Syntheses of multihalogenated 9,10-diphenylanthracenes as “abnormal” products of the McMurry reaction.

Compared with “normal” products from McMurry reactions under similar conditions, the formation of those halo-substituted DPA derivatives is rather unexpected, and the 2-halo-substituted benzophenone skeleton of the substrates should play a key role. One possible mechanism for the formation of those “abnormal” products is proposed in Scheme 4.

It is inferred that the treatment of 2-halo-substituted benzophenones (**1a** and **1b**) with low-valent titanium species generated from TiCl_4 and zinc dust gives diradical species, which undergo nucleophilic attack immediately with unreacted 2-halo-substituted benzophenones to form 9,10-diphenyl-9,10-dihydroanthracene-9,10-diol derivatives. Subsequent deoxygenation gives **DPA1a** and **DPA1b** (path I). The diradical species are also subject to self-dimerization to afford **DPA** (path II). The diradical species that are generated initially should react with substrates **1a** and **1b** more efficiently. Therefore, path I is the major reaction route, and thus the yields of **DPA1a** and **DPA1b** are much higher than that of **DPA**. 2,5-Halo-substituted benzophenones react through the same mechanisms to afford the major products **DPA3a–DPA3c** with the minor product **DPA2**. Because of the electron-withdrawing effect of the additional halogen atom at the 5-position of phenyl ring, the diradical species that are generated from 2,5-halo-substituted benzophenones become more stable than those generated from 2-halo-substituted ones, which results in higher yields of **DPA3a–DPA3c** compared with **DPA1a** and **DPA1b**.

The molecular packing patterns of **DPA1a**, **DPA2**, and **DPA3a** are shown as examples in Figure S2–S4 in the Supporting Information. It can be seen that the number of halogen atoms on the DPA framework has remarkable impact on the packing patterns of these DPA derivatives in the crystalline state. Replacement of the halogen atoms with other functional groups could easily modulate the electronic structure and photophysical properties as well as aggregation format of the materials in the solid state. The optical properties of these DPA derivatives were measured in dilute THF solutions (10 μM). The results reveal that these compounds have similar absorption spectral profiles, with absorption maxima in the range of 394–403 nm (Figure S5A in the Supporting Information), which are associated with the $\pi\text{--}\pi^*$ transition of the molecule. Intense blue fluorescence peaks at 427–435 nm were recorded (Figure S5B) for these DPA derivatives. The halogen atoms at the C2

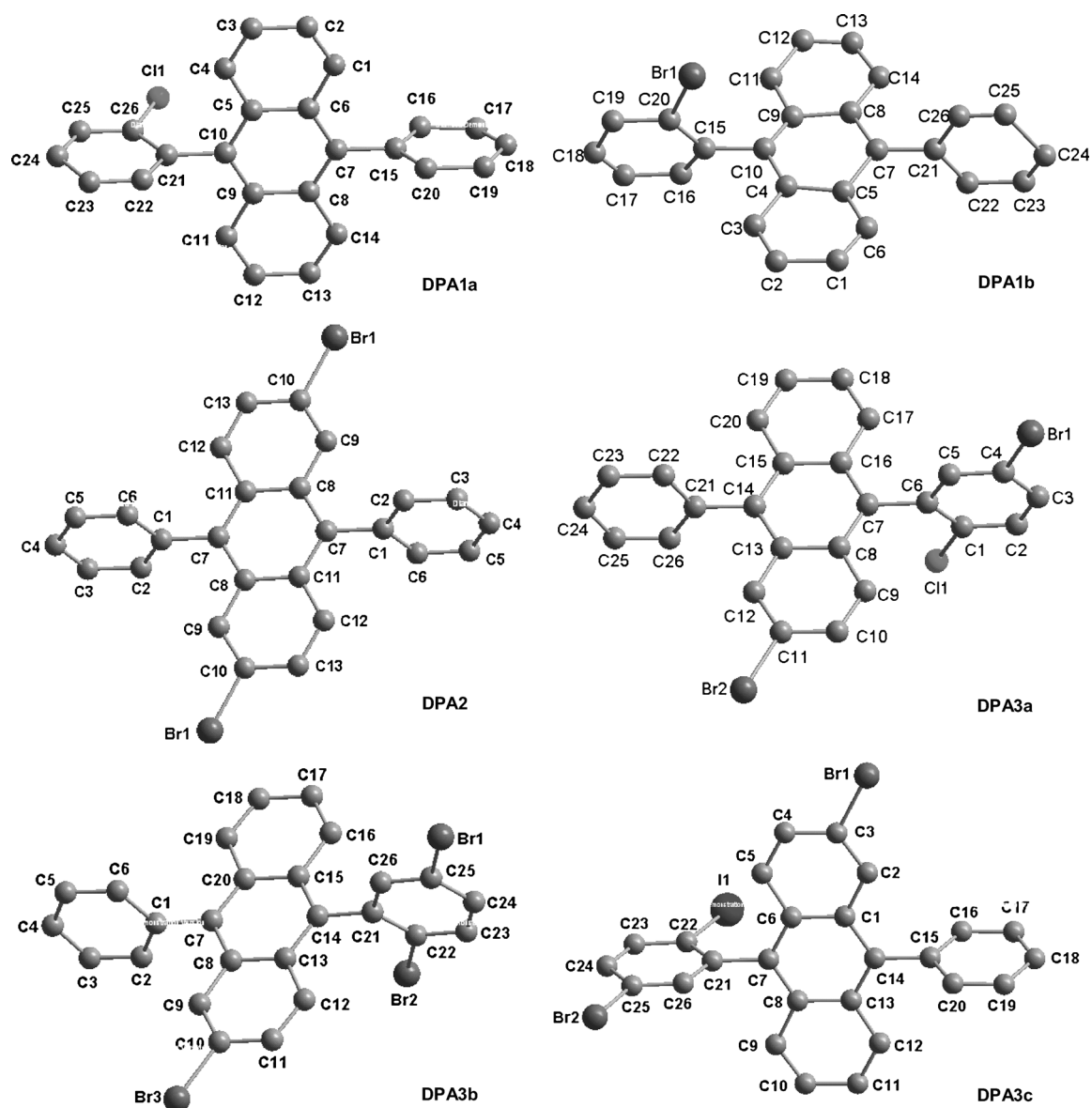


Figure 1. The X-ray determined molecular structures of **DPA1a**, **DPA1b**, **DPA2**, **DPA3a**, **DPA3b**, and **DPA3c**. Hydrogen atoms are omitted for clarity.

and C6 positions of the anthracene ring lead to a slight redshift in the absorption and photoluminescence spectra in comparison with the halogen atoms on the phenyl rings.

In summary, a facile approach to construct molecules with DPA frameworks has been developed. Various halo-substituted DPA derivatives were prepared from 2- and 2,5-halo-substituted benzophenones in one step in the presence of TiCl_4 and zinc dust. These compounds are totally different from the “normal” products of McMurry reactions, which paves a new avenue for the synthesis of DPA derivatives. The results presented here are also different from the limited unusual courses of McMurry reactions that give large polycyclic aromatic hydrocarbons.^[13] Systematic investigations on the applicability of this reaction based on many analogous substrates are in progress. Meanwhile, lumines-

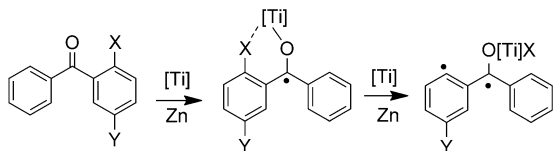
cent materials for OLEDs based on these new DPA derivatives are being prepared.

Experimental Section

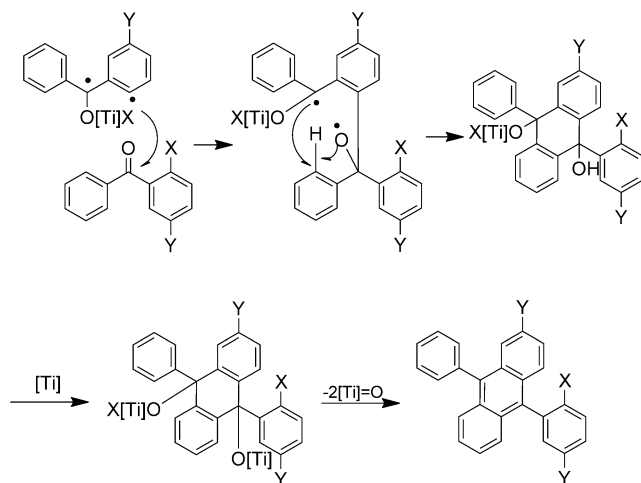
General Procedure for the Synthesis of Halo-Substituted DPA

TiCl_4 (1.2 mmol) was added dropwise to a mixture of 2- or 2,5-halo-substituted benzophenone (1 mmol) and zinc dusts (10 mmol) in dry THF (15 mL) under nitrogen at -78°C . After the addition of TiCl_4 , the reaction mixture was stirred for 15 min at -78°C , then warmed to room temperature and stirred for another 15 min. The reaction mixture was then heated to reflux for 8 h. After filtration and solvent evaporation, the residue was purified by chromatography on a silica-gel column with hexane/dichloromethane as eluent to afford the products.

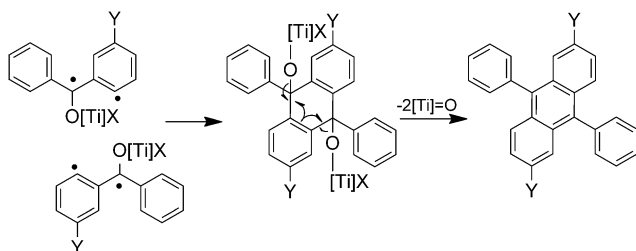
Formation of diradical species:



Path I: nucleophilic attack of diradical species on C=O bond.



Path II: self-dimerization of diradical species.



Scheme 4. Proposed mechanism for the formation of DPA derivatives. X = Cl, Br, or I; Y = H, or Br.

X-ray Diffraction Analysis Data

CCDC 889534 (**DPA1a**), 889535 (**DPA1b**), 870963 (**DPA2**), 889536 (**DPA3a**), 870964 (**DPA3b**), and 870965 (**DPA3c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <http://www.ccdc.cam.ac.uk/data%5frequest/cif>.

DPA1a

$C_{26}H_{17}Cl$; $M = 364.85$; monoclinic; Pc ; $a = 11.5377(16)$; $b = 7.8535(11)$; $c = 11.8257(16)$ Å; $\beta = 115.637(2)$; $V = 966.1(2)$ Å³; $Z = 4$; $\rho_{\text{calc}} = 2.509$ g cm⁻³; $\mu = 0.409$ mm⁻¹ ($M_{\text{O}_{K\alpha}}$, $\lambda = 0.71073$); $F(000) = 760$; $T = 293(2)$ K; 6150 measured reflections; 3575 independent reflections ($R_{\text{int}} = 0.0210$); GOF on $F^2 = 1.311$; $R_1 = 0.1368$; $wR_2 = 0.2957$ (all data); Δe 1.651 and -0.302 e Å⁻³.

DPA1b

$C_{26}H_{17}Br$; $M = 409.31$; monoclinic; Pc ; $a = 11.472(2)$; $b = 7.7813(13)$; $c = 12.188(2)$ Å; $\beta = 116.190(3)$; $V = 976.3(3)$ Å³; $Z = 4$; $\rho_{\text{calc}} = 2.785$ g cm⁻³; $\mu = 4.224$ mm⁻¹ ($M_{\text{O}_{K\alpha}}$, $\lambda = 0.71073$); $F(000) = 832$; $T = 293(2)$ K; 6285 measured reflections; 3192 independent reflections ($R_{\text{int}} = 0.0345$); GOF on $F^2 = 1.400$; $R_1 = 0.1616$; $wR_2 = 0.3718$ (all data); Δe 0.614 and -1.058 e Å⁻³.

DPA2

$C_{26}H_{16}Br_2$; $M = 488.20$; monoclinic; $P2_1/c$; $a = 10.7905(14)$; $b = 15.832(2)$; $c = 5.8309(7)$ Å; $\beta = 96.579(2)^\circ$; $V = 989.6(2)$ Å³; $Z = 4$; $\rho_{\text{calc}} = 1.638$ g cm⁻³; $\mu = 4.105$ mm⁻¹ ($M_{\text{O}_{K\alpha}}$, $\lambda = 0.71073$); $F(000) = 484$; $T = 296(2)$ K; 8429 measured reflections; 2271 independent reflections ($R_{\text{int}} = 0.0242$); GOF on $F^2 = 1.022$; $R_1 = 0.0386$; $wR_2 = 0.1266$ (all data); Δe 0.466 and -0.223 e Å⁻³.

DPA3a

$C_{26}H_{15}Br_2Cl$; $M = 522.65$; triclinic; $P\bar{1}$; $a = 8.2217(5)$; $b = 11.0100(5)$; $c = 13.0022(5)$ Å; $\alpha = 74.308(4)$; $\beta = 80.816(4)$; $\gamma = 69.425(4)^\circ$; $V = 1058.11(8)$ Å³; $Z = 2$; $\rho_{\text{calc}} = 1.640$ g cm⁻³; $\mu = 3.967$ mm⁻¹ ($M_{\text{O}_{K\alpha}}$, $\lambda = 0.71073$); $F(000) = 516$; $T = 296(2)$ K; 7021 measured reflections; 3863 independent reflections ($R_{\text{int}} = 0.0273$); GOF on $F^2 = 1.041$; $R_1 = 0.0783$; $wR_2 = 0.1345$ (all data); Δe 0.855 and -0.554 e Å⁻³.

DPA3b

$C_{26}H_{15}Br_3I$; $M = 567.11$; triclinic; $P\bar{1}$; $a = 8.2522(11)$; $b = 11.0428(15)$; $c = 13.1003(18)$ Å; $\alpha = 74.589(3)$; $\beta = 80.480(3)$; $\gamma = 69.189(3)^\circ$; $V = 1072.4(3)$ Å³; $Z = 2$; $\rho_{\text{calc}} = 1.756$ g cm⁻³; $\mu = 5.652$ mm⁻¹ ($M_{\text{O}_{K\alpha}}$, $\lambda = 0.71073$); $F(000) = 552$; $T = 296(2)$ K; 17 641 measured reflections; 4891 independent reflections ($R_{\text{int}} = 0.0256$); GOF on $F^2 = 1.076$; $R_1 = 0.0635$; $wR_2 = 0.1513$ (all data); Δe 1.453 and -0.758 e Å⁻³.

DPA3c

$C_{26}H_{15}Br_3I$; $M = 614.10$; triclinic; $P\bar{1}$; $a = 8.1190(14)$; $b = 11.0489(19)$; $c = 13.905(2)$ Å; $\alpha = 96.922(3)$; $\beta = 105.375(3)$; $\gamma = 110.024(3)^\circ$; $V = 1098.8(3)$ Å³; $Z = 2$; $\rho_{\text{calc}} = 1.856$ g cm⁻³; $\mu = 5.103$ mm⁻¹ ($M_{\text{O}_{K\alpha}}$, $\lambda = 0.71073$); $F(000) = 588$; $T = 296(2)$ K; 14 612 measured reflections; 3868 independent reflections ($R_{\text{int}} = 0.0240$); GOF on $F^2 = 1.193$; $R_1 = 0.0488$; $wR_2 = 0.1491$ (all data); Δe 1.407 and -1.037 e Å⁻³.

Acknowledgements

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