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Paraphenylene dimers with diphenylamine donor groups: synthesis and photophysics

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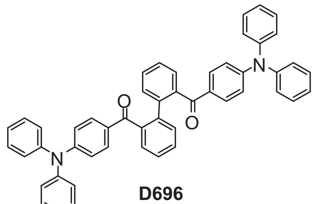
ABSTRACT

A novel paraphenylene dimer (**D696**) with electron donating diphenylamine side chain groups has been prepared. Optical absorption measurements were theoretically and experimentally determined showing a red shift in the absortivity relative to dialkylamine functionalized benzophenone dimers. The fluorescence of **D696** was quenched in a concentration dependent manner in the presence of reduced graphene oxide (RGO).

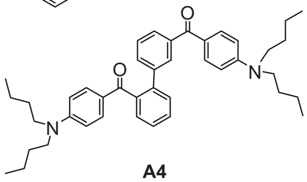
The large absorption coefficients, high charge mobility, excellent thermal and mechanical stability, and affordable large scale production costs of semiconducting polymers position these materials to outperform their silicon-based counterparts for application in light emitting diodes, photovoltaic devices, and nonlinear optics.[1–5] However, applications have not been fully realized due to charge transport inefficiencies in these materials.

Polyparaphenylenes and oligomeric paraphenylenes (OPPs) have lagged behind other semiconductor materials because of intrinsic limitations in flexibility, symmetry breaking, or distortion properties, and hole injection difficulties as a result of high HOMO levels. These limitations can be addressed by the selective introduction of sterically demanding and electronically rich or favorable substitution groups.

We and others continue to show an interest in model paraphenylene oligomers derivatized with donor and acceptor groups for the study of photoinduced charge transfer.[6–11] Our previous experimental and theoretical substitution strategies involved the formation of butyl amine side chain groups.[6] In those studies, we demonstrated the potential to red shift the theoretical band gap of paraphenylene based dimers by the substitution of electron donating groups including various alkyl amine and diphenyl amine units. While earlier studies report that the spectral absorption and emission of oligomeric semiconductors are influenced by structural modification arising from the introduction of different electron donating and withdrawing groups,[12–14] confirmation of our promising theoretical results with OPP functionalized with diphenylamine donor groups was previously unobtainable as the dimers were not synthetically available. We describe here the synthesis of the 4-(*N*,*N*-diphenylamino)benzoyl substituted paraphenylene dimer (**D696**). The structure of **D696** is illustrated and compared with the dibutylamino substituted dimer **A4** reported earlier (Fig. 1). Important issues that we address in this work include the role of the substitution chemistry on the absorption and emission properties of the dimer. In addition, we address the role of coupling the dimers in a head-to-head (HH) conformation where the dimer contains a mirror plane of symmetry upon the union of the monomers (i.e., the two carbonyl groups face each



D696



A4

Figure 1. Structures of paraphenylene dimers derivatized with the donor group diphenylamine (**D696**) and dibutylamine (**A4**).

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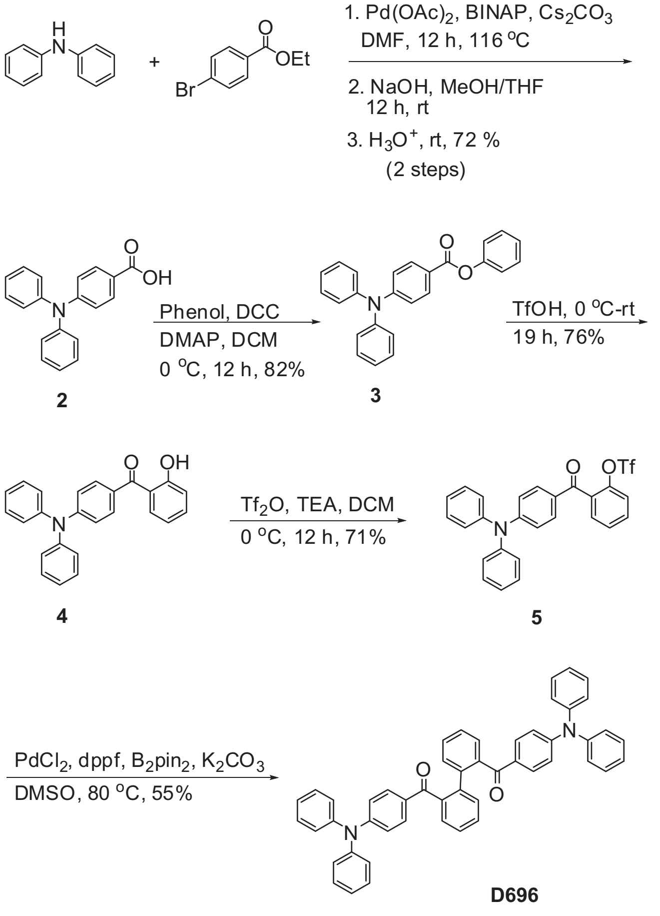
other in a planar view of the dimer). Furthermore, we observe efficient quenching of the fluorescence of **D696** by reduced graphene oxide, a photo-induced electron transfer process reported in the literature.[15]

As shown in Scheme 1, the synthesis of **D696** was accomplished in six-steps (see Supplementary data). Briefly, diphenylamine was coupled with ethyl 4-bromobenzoate by using the Buchwald amination chemistry.[16] The resulting yellow viscous oil underwent alkaline hydrolysis[17] to provide the corresponding acid as a white solid in 72% yield for two-steps. Subsequent reaction with phenol in the presence of DCC and DMAP produced the ester **3** in good yield. Initial attempts to convert the ester **3** into the ketone **4** using a Fries rearrangement reaction with Lewis acids such as $AlCl_3$, scandium triflate, and $BF_3{\cdot}OEt_2$ in different solvents resulted in poor yields.[18] The rearrangement was however successfully carried out, in a yield of 76%, when the reaction was performed in neat triflic acid at 0 °C followed by warming to room temperature. Finally, the hydroxyl group of **4** was activated by triflic anhydride to produce triflate **5** which was then dimerized in the presence of a palladium catalyst to afford **D696** as a yellow solid in 55% yield.

The redox behavior of **D696** was investigated by cyclic voltammetry (CV). The studies were performed using a solution of **D696** (1.64×10^{-4} M) prepared in DMF with n-Bu_4NPF_6 (0.1 M) as a supporting electrolyte. As shown in Figure 2, the dimer exhibits a reversible anodic wave at ~0.75 V versus $AgNO_3$/Ag which is attributed to the electron donating tendency of the diphenylamine group. The energy associated with this oxidation is taken to be the HOMO energy level. **D696** exhibits no observable cathodic wave. Thus, the LUMO energy level of **D696** was calculated by subtracting the HOMO energy level and the zeroth–zeroth energy (E_{0-0}) extrapolated from the intersection between the absorption and emission spectra (see Fig. S1 in Supplementary data).



Scheme 1. Synthesis of **D696**.

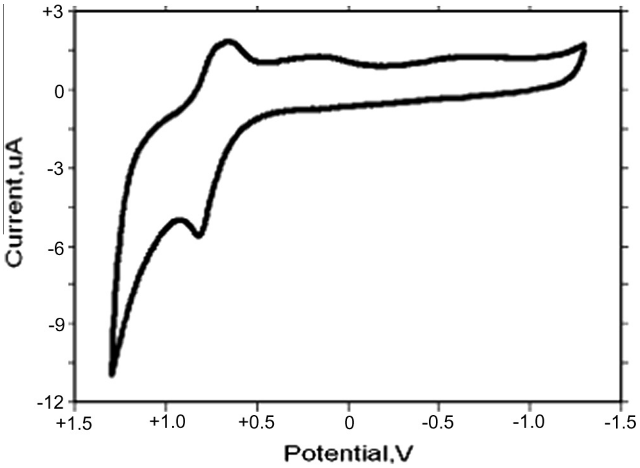


Figure 2. CV curve of **D696** in acetonitrile.

The absorption spectra of **D696** taken in DMF solution at a concentration of 5.49×10^{-5} M is shown in Figure 3. This is very close to our theoretically determined UV–vis spectra previously reported for diphenylamine functioned OPP.[6] The spectrum features a relatively broad absorption in the ultraviolet and slight trailing in the visible region with maxima of 290 nm and 368 nm. These two intense absorption maxima suggest π–π* transition and intramolecular charge transfer between the diphenylamine donor group and the carbonyl group which acts as a modest acceptor.

The absorption, emission, and electrochemical properties of **D696** are listed in Table 1. From our experimental data, we calculated the band gap of **D696** to be 2.90 V. This band gap is lower than unsubstituted paraphenylene and polypyrrole (3.1 eV) but higher than other polymers such as polythiophene and poly(2-vinylpyridine).

The geometry of the ground state molecular orbitals of **D696** was fully optimized by the density functional theory (DFT) with Becke's three-parameter (B3) exchange functional along with the Lee–Yang–Parr (LYP) nonlocal correlation functional implementing the modest 6-31G(d,p) basis set. The calculations were carried out in WebMO environment interfaced with GAUSSIAN 94/98/03 software package. The plots of the HOMO and LUMO of the dimer are given in the Supplementary data (Fig. S2) and the respective electron densities images are presented in Figure 4. The absorption spectra

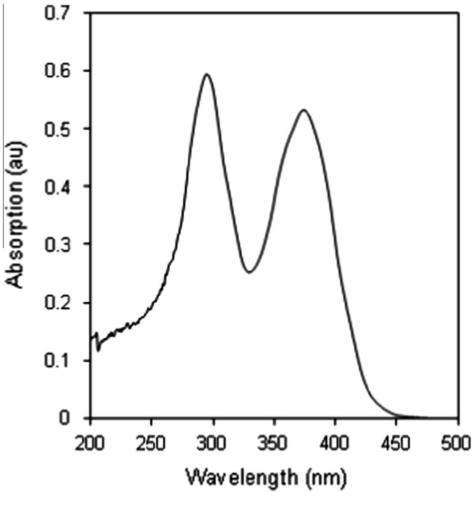


Figure 3. Absorption spectra of **D696** in DMF.

Table 1
Absorption, emission, and electrochemical properties of **D696**

Absorption[a] λ_{max} (nm)	Emission[a] λ_{em} (nm)	Oxidation potential data[b]		
		E_{0-0}[c] (V)	E_{ox} (V)	$E_{\text{ox}} - E_{0-0}$ (V)
368	534	−2.15	0.75	2.90
290	–	–	–	–

[a] Absorption and emission spectra were measured in DMF solution at room temperature.

[b] The oxidation potential was measured in acetonitrile with 0.1 M tetrabutylammonium hexfluorophosphate (Bu_4NPF_6) as the supporting electrolyte (working electrode: glassy carbon; counter electrode: Pt wire; reference electrode: Ag/Ag^+).

[c] E_{0-0} was estimated from the onset point of absorption spectra.

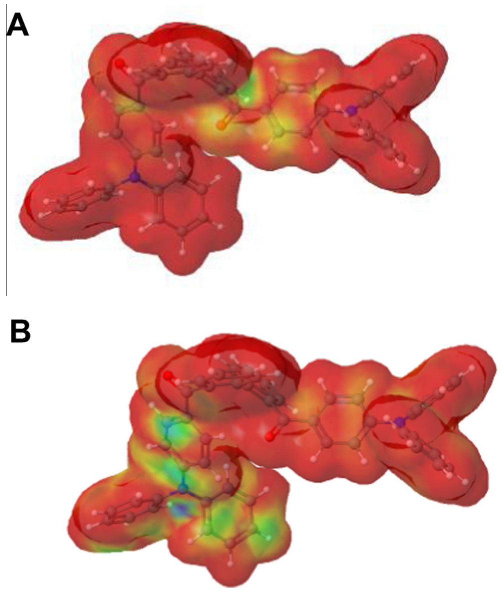


Figure 4. Molecular orbitals of **D696**: (A) LUMO; and (B) HOMO.

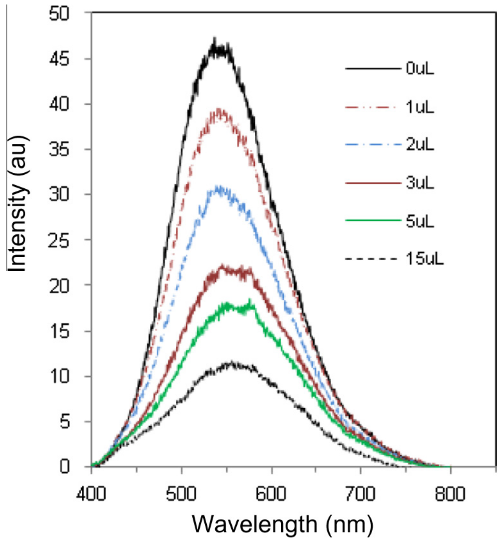


Figure 5. Quenching of the fluorescence of 0.05 mM **D696** in DMF (2.8 mL) recorded during addition of an DMF suspension of 0.8 mg/mL RGO (0–15 μL).

of **D696** have two features and the dominate absorption band is observed at 3.36 eV (369 nm). The second transition is observed at 5.00 eV (248 nm). The dominance of these features is reversed in the theoretical calculations previously reported by our group on the head to tail union of the diphenylamine OPP monomer. This suggests that the gas phase computational models really should be altered to include solvent effects that would average the rotational energies sampled by the phenyl rings of the donor.

The increase in the absorption wavelength of **D696** relative to **A4** is due to the extension of π-electron conjugation in the molecule with the addition of the two phenyl groups. It is important to note that the HOMO and LUMO molecular orbitals show localized electron density on the diphenylamine and carbonyl units, respectively. It is noteworthy that the LUMO electron density of **D696** is located primarily on the carbonyl group, suggesting the excited electron can be quenched by an efficient electron trap.

To probe the interaction between the excited-state of **D696** and the reduced graphene oxide (RGO) in solution, fluorescence spectra of **D696** at different RGO concentrations were recorded. The intensity of the **D696** fluorescence bands decreases with the increase in RGO concentration as illustrated in Figure 5. This confirms a strong interaction between the **D696** and RGO and is presumably due to an excited state phenomenon since we do not observe ground state charge-transfer in the absorption spectra of the physically mixed **D696**/RGO solution. In fact, the two absorbance bands of **D696** increase in intensities with the graphene oxide concentration (see Fig. S3 in Supplementary data) and this is expected due to the increasing intensity of the graphene oxide absorption band around 230 nm. We also do not see new absorption bands attributable to charge-transfer.

Quenching of fluorescence of aromatic molecules by RGO has been observed in porphyrin,[19] porphyrin-fullerene/nanohorn[20,21], and pyrene carbon nanotube systems.[22] Both electron transfer and energy transfer have been suggested to explain the fluorescence quenching.[23] Additional studies are required to determine the mechanism of fluorescence quenching observed in our system. We can conclude that RGO acts as an efficient acceptor for the photoinduced charge separated species produced in **D696**. This feature could be exploited in the design of photovoltaic cells.

In summary, we have synthesized a novel paraphenylene dimer, **D696** and shown its absorption, emission, and electrochemical properties. We found the band gap of **D696** to be 2.90 V, which is relativity high for the application of solar cells directly but by adding a strong π-acceptor the band gap could be lowered.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.03.141.

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