

Synthesis and Photophysics of Dibenz-*[a,c]*phenazine Derivatives

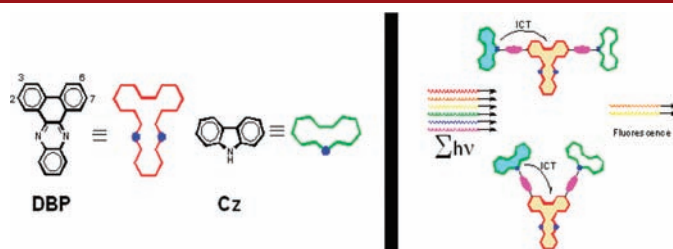
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ABSTRACT

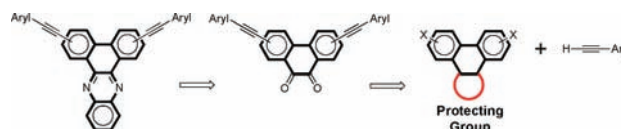


The synthesis of dipolar dibenz[*a,c*]phenazine (DBP) derivatives is described. The compounds possess little electronic communication between donor and acceptor units in the ground state regardless of the pattern of substitution. The dipolar derivatives deactivate mostly via electron transfer (eT) under polar conditions. Intersystem crossing is likely to compete for S₁ relaxation.

Dibenz[*a,c*]phenazine (DBP) is a structural analogue of the expensive and rare hydrocarbon dibenz[*a,c*]anthracene.¹ Its synthesis via condensation of *o*-diaminobenzene with phenanthrene-9,10-dione (PD) has triggered interest in the optical and conductive properties of some of its derivatives.² After the realization of columnar phase control in thin films and solid–liquid interfaces of large polyaromatic hydrocarbons,³ most of the latest reports on DBP derivatives (DBPDs) focus on applications as liquid crystals.² Consequently, improvement of their optical properties via chemical modification are scarce.^{4–6} Derivatization of DBP is promising given its skeletal rigidity,

electron affinity, and thermal stability. Establishing design patterns for its better use in organic electronics is desirable. To answer these questions, the synthesis of dipolar DBPDs via incorporation of pendant carbazole (Cz) to the DBP acceptor linked through phenylacetylene (PA) was pursued. Cz-lacking compounds were also synthesized for comparison purposes.

Scheme 1. Initial Synthetic Approach to DBPDs



Preparation of DBPDs was planned around the expected high-yield condensation of *o*-diaminobenzene with a suitable PD derivative (Scheme 1).⁷

PD derivatization via Pd-catalyzed C–C coupling is known to be problematic.^{8,9} However, Tour circumvented this issue by protecting the carbonyl groups with ethylene

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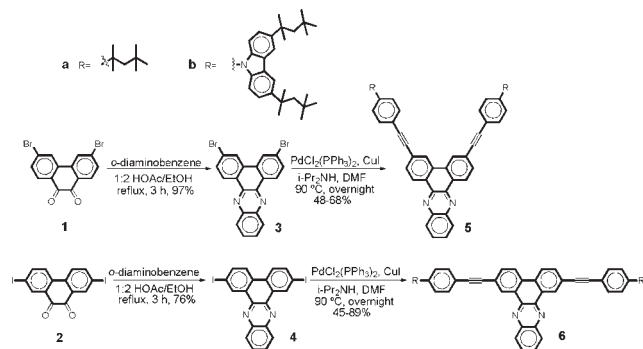
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glycol under acid conditions prior to Pd coupling.¹⁰ Subsequent deprotection permits recovery of the dihalophenanthrene-9,10-dione (DHPD) functionality. Müllen reported a similar approach when PD was functionalized with Si-terminated acetylenes: protection of DHPD with Me₂SO₄, Sonogashira coupling, and regeneration of the *o*-quinone with CAN.¹¹

Scheme 2. Final Synthesis of DBP Derivatives



While PA is compatible with Tour's protocol, the introduction of soluble CPA units leads to problematic regeneration of PD even with the use of strong acids such as CF₃CO₂H or TfOH. This drawback prompted us to try an alternative based on Müllen's protocol. We also found that the solubility of DBP was improved after incorporation of *tert*-octyl groups in the phenyl and Cz units of the coupling partners. Regeneration of the PD unit with CAN is difficult for Cz-containing compounds as well. These results suggest that incorporating electron-rich heterocycle derivatives in conjugation to PD might be inefficient in a general sense.

The early derivatization of DHPD producing dihalodibenzo[*a,c*]phenazine (DHDBP) was effective for further access of dipolar DBPDs. Tour and Jenekhe were able to synthesize DBPDs via Pd-catalyzed cross-coupling reactions in high yields.^{4,10} This counterintuitive finding suggests that the poor solubility of DHDBP is irrelevant in order for the reaction to proceed. Consequently, Cz units were incorporated through this method after the synthesis of convenient building blocks (Scheme 2).

Voltammetry experiments (CV and DPV) vs Fc/Fc⁺ reveal that all DBPDs possess one single-electron reduction wave and, only for the case of Cz-substituted variants, one reversible oxidation wave within the region scanned (Figure S9, Supporting Information). This suggests localization of the LUMO in the DBP unit. The ionization potential and electron affinity values could be taken as references for the HOMO and LUMO energies for all

DBPDs (Table 1). All EA values were found to be remarkably similar to that of parent DBP.¹²

Table 1. Redox Potentials of DBPDs in DMF vs Fc/Fc⁺

compd	$E_{1\text{red}}^0$ (V)	E_{pa} (V)	IP (eV)	EA (eV)
PADBP27	-1.61		>5.7	3.3
CPADBP27	-1.64	+0.74	5.6	3.3
PADBP36	-1.65		>5.7	3.3
CPADBP36	-1.62	+0.79	5.7	3.3
DBP				3.1 ⁴

All DBPD/THF solutions absorb light strongly at $\lambda < 450$ nm (Figure 1A, $\log(\epsilon_{\text{abs}}) \sim 4.48-4.84$ at λ_{max}). PADBP27 exhibits two absorption bands with maxima centered at 335 and 395 nm, respectively. The features of the CPADBP27 spectrum resemble the coalescence of the two absorption bands of PADBP27. In contrast, the spectral features of 3,6-DBPs are similar to each other. The only difference among these is the slightly red-shifted absorption of CPADBP36's red-edge. These observations underline the small electronic contribution of Cz on the band gap of the low energy transitions, although the oscillator strengths are evidently enhanced by the expansion of the π -system. Solvatochromic effects in the absorption spectrum were negligible, in parallel to parent DBP (Figure S10, Supporting Information). This reflects small GS dipole moments for the compounds.

Steady-state photoluminescence (PL) measurements on a PADBP36/THF solution showed a narrow and structured signal in contrast to all other DBPDs (Figure 1B). The significant red shift between CPADBP36 and PADBP36 in THF reflects either important internal reorganization or S₁ energy stabilization due to solvation after incorporation of Cz donors. Poor solubility of DBPDs in cyclohexane and other aliphatic solvents restricted the calculation of their internal reorganization energies. Most DBPDs exhibit dual emission from the local excited (LE) and charge transfer (CT) states (Figure S11, Supporting Information). This is evident for the cases of PADBP27, CPADBP27, and CPADBP36, where the CT band develops in parallel with the increasing of solvent polarity. The lack of PL signal in the case of both variants of CPADBP in DMF solution highlights an efficient nonradiative decay (NRD) mechanism. The nature of this NRD is uncertain, although charge separation (CS) could occur at such a high polarity. Similar systems with different acceptors behave this way.¹³ Lippert–Mataga plots (LMPs) reflect nonlinear dependence of the Stokes shift with the Onsager solvent parameter $f(\epsilon, n)$ for DBPs (Figure S12, Supporting Information).

(12) Assuming Koopmans' theorem is valid, the values of interest were calculated using $\text{EA (eV)} = E_{\text{onset}}(\text{red}) + 4.9$; $\text{IP (eV)} = E_{\text{onset}}(\text{ox}) + 4.9$. These formulas are based on the assumptions that the energy level of SCE relative to vacuum is 4.4 eV and SCE reference with respect to Fc/Fc⁺ is +0.5 V.

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Table 2. Photophysical Properties of DBPDs Recorded in Toluene and THF at Room Temperature after Photoexcitation at 370 nm

compd	λ_{em} (nm)	toluene				THF				
		τ_{em}^1 (ns)	Φ_F^a	k_{rad} ($\times 10^7$ s $^{-1}$)	k_{nrad} ($\times 10^7$ s $^{-1}$)	τ_{em}^1 (ns)	τ_{em}^2 (ns)	Φ_F^a	k_{rad} ($\times 10^7$ s $^{-1}$)	k_{nrad} ($\times 10^7$ s $^{-1}$)
PADBP27	500	2.44	0.106	4.3	36.6	4.29		0.124	2.9	20.4
CPADBP27	600	3.35	0.177	5.3	24.6	3.64 (3%)	25.6 (97%)	0.237	0.9 ^b	3.0
PADBP36	420	<1.00	0.090	>9.0	>91.0	<1.00		0.135	>13.5	>86.5
CPADBP36	600	1.49	0.229	15.4	51.7	13.4 (70%)	19.2 (30%)	0.304	2.3 ^b	5.2

^a Φ_F values against coumarin 153 in EtOH ($\Phi_F = 0.73$). ^b Value calculated from the PL lifetime of biggest contribution.

While the linear model reveals higher dipole moment differences between the ground and excited state of CPADBP36 with respect of the 2,7-variant, the opposite was found for PADBPs.

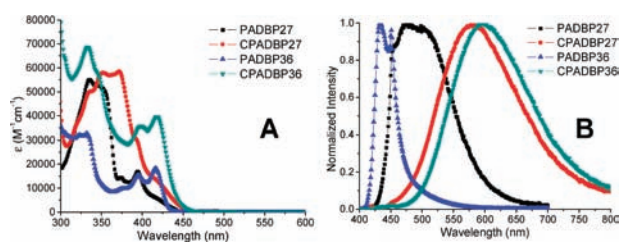


Figure 1. (A) Normalized UV–vis absorption spectrum of solutions of PzDs in THF at 25 °C. (B) Normalized PL spectra of THF solutions of FMDs at 25 °C after excitation at 400 nm.

The PL lifetimes of DBPDs, as well as the Φ_F values in toluene and THF solutions at room temperature, are reported in Table 2. The PL of DBPDs followed mono-exponential decay in toluene, while both Cz-containing variants presented biexponential decay in THF in the nanosecond time regime. Given that solvatochromic behavior from DBPDs is important for the cases of 2,7-DBPDs and CPADBP36, as well as the observation that PADBP27 presents monoexponential decay in THF, there could be an equilibration between LE and CT states in the case of dipolar DBPDs. The shorter lifetime component is minor for CPADBP27, contrary to its 3,6-variant in THF. On the other hand, the rapid NRD found for PADBP36 might be explained in terms of a very fast intersystem crossing (ISC) possibly mediated by an upper $n-\pi^*$ state. This is based on the negligible solvatochromic effects observed in this system (i.e., no CT occurs in this compound) plus the fact that the rigidity of the DBPD acceptor implies minuscule vibrational coupling between states.

The ionization potential of Cz (IP = 5.3 eV)¹⁴ and electron affinity of Pz (EA = 3.1 eV)⁴ have been reported in acetonitrile ($\epsilon_S = 37$). Assuming solvent separated ion-pair (SSIP) formation, analysis of the driving force for

electron transfer (eT) was performed via the Rehm–Weller equation.^{15,16} The 0–0 singlet gap of the donor ($E_{S1} = 84$ kcal/mol)¹⁷ and that of the acceptor ($E_{S1} = 71$ kcal/mol)⁶ revealed exergonic driving forces for charge separation (CS) in these compounds, resulting in -27 and -14 kcal/mol in a solvent of medium polarity such as THF. The center-to-center distance is assumed to be 1.3 nm, and the radii for Cz and DBP are taken as 3.5 and 4.0 Å, respectively, after evaluation of their optimized geometries via DFT calculations (Section S3, Supporting Information). Therefore, SSIP formation should occur in the proposed DBPDs if their singlet energies are high enough, the kinetic barriers are not sufficiently high, or the competing deactivation mechanisms (i.e., PL or ISC) are not significantly faster. While this should favor CT as excited-state deactivation mechanism in all dipolar DBPDs, ISC is yet to be discarded given that the spin–orbit coupling in these systems should be similar as it is dominated by the nature of the acceptor unit.

After evaluation of the optimized geometries at the B3LYP/6-31G* level, it was found that the PA bridges are planar to the acceptor unit in all cases. In the case of CPADBPs, the Cz donors were tilted from the PADBP plane. The frontier orbitals of CPADBPs (Figure 2) reveal HOMOs localized on both CPA units and the LUMOs on the DBP acceptor. This points toward CT character for HOMO→LUMO transitions. The calculated ground-state (GS) dipoles resulted are low for both dipolar compounds (CPADBP27, $\mu_{S0} = 0.20$ D; CPADBP36, $\mu_{S0} = 1.92$ D) as expected from their symmetry. The calculated difference between excited and ground state dipole moments via TDDFT is significant for both compounds, especially for the case of CPADBP36 (CPADBP27, $\Delta\mu = 12.9$ D; CPADBP36, $\Delta\mu = 38.1$ D). This anticipates that if the molecule experiences small internal reorganization energies, the S_1 state energy will be dependent on the solvent reorganization. TDDFT also reveals that the extension of the π -system negligibly affects the $n-\pi^*$ transitions while decreasing the energy gap of the $\pi-\pi^*$ transitions. This is more evident when incorporating Cz units. For both PADBP variants, the $S_3 \leftarrow S_0$ transition is mapped as an

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$n-\pi^*$ with energies relatively close to the $S_1 \leftarrow S_0$ transition, which is $\pi-\pi^*$ ($\Delta E \sim 7.1-14.5$ kcal/mol range). However, while CPADDBPs possess $n-\pi^*$ transitions of the same energy as those from PADDBPs, there are many $\pi-\pi^*$ transitions of lower energy gap in between the $\pi-\pi^*$ (S_1) and the $n-\pi^*$ (S_n) states.

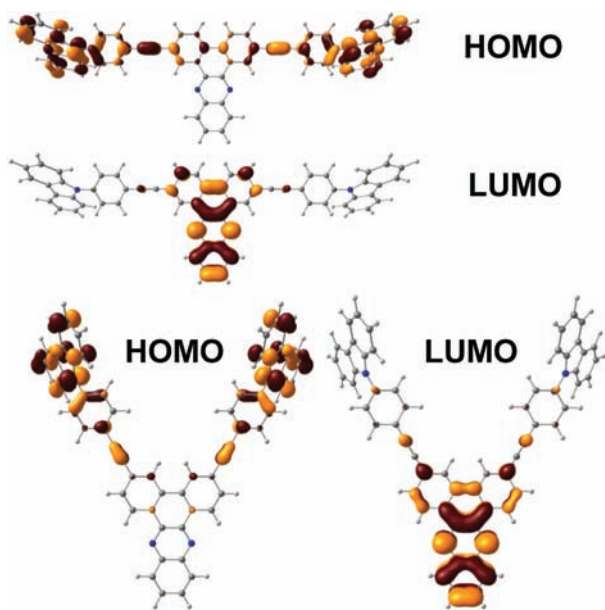


Figure 2. Frontier orbitals of optimized dipolar DBPDs computed at the B3LYP/6-31G* DFT level (isodensity = 0.03).

Initial studies on DBP by Hochstrasser focused on oscillator strengths for the $n-\pi^*$ transition in single crystals at low temperatures (4.1 and 77 K).¹⁸ While DBP's lowest $n-\pi^*$ and $\pi-\pi^*$ states are close in energy, the $n-\pi^*$ transition possibly localizes in the region of the positive hole at the nitrogen. This is based on the spectral similarities between phenazine (Pz) and DBP. The negligible fluorescence from Pz highlights effective ISC ($k_{ISC} \sim 10^{12}$ s⁻¹).^{19,20} This is also apparent in DBP ($\Phi_F \sim 1\%$)¹⁹ and could consequently apply to some DBPDs studied herein

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based on our DFT data (vide supra). The appearance of plane polarized phosphorescence had been attributed to an out-of-plane ring deformation mode²¹ implying the participation of an $n-\pi^*$ intermediate state.²² Later studies via ps laser flash photolysis (LFP) labeled this ISC transition as $S_1(n-\pi^*) \rightarrow T_1(\pi-\pi^*)$.²³ However, assigning S_1 as $n-\pi^*$ state seems inappropriate if considering the negligible UV-vis solvatochromic shifts of DBP²⁴ and DBPDs. Davis assigned the S_1 of DBP as $\pi-\pi^*$ in the early 1970s after studying the photoreduction of DBP with tri-*n*-butylstannane.²⁵ Such an assignment was supported by others,^{24,26-28} and on the basis of our observations, we find it appropriate for our systems. Interestingly, many mechanisms seem to be actively competing in all dipolar DBPDs, wherein polar media CT deactivation is favored in all cases.

In summary, novel dipolar compounds based on Cz donors and a DBP acceptor were synthesized and their photophysics characterized. The compounds possess small electronic communication between D-A units in the ground state. The S_1 state of dipolar DBP derivatives deactivate mostly nonradiatively via charge transfer under polar conditions.

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Supporting Information Available. Synthetic procedures, compound characterizations, and ¹H and ¹³C NMR data. Cartesian coordinates of DBPD-optimized geometries, TDDFT data, and orbital maps. Cyclic and differential pulse voltammograms. UV-vis absorption and PL spectra in solvents of varied polarity. Lipert-Mataga plot. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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