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A Push–Pull Macrocycle With Both Linearly Conjugated and Cross-Conjugated Bridges

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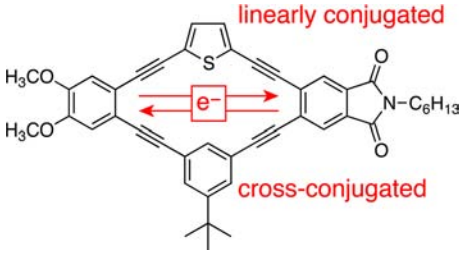
ABSTRACT



A series of shape-persistent macrocycles featuring both *m*-phenylene and 2,5-thiophene linkers has been synthesized, including an example where they bridge electron-rich (veratrole) and electron-poor (phthalimide) units. Charge transfer in this "push–pull macrocycle" has been investigated by UV–vis and fluorescence spectroscopies and DFT calculations. The effect of pairing structurally distinct conjugated bridges is discussed in the context of acyclic and symmetrical macrocyclic analogs.

Despite long-standing interest in one-dimensional (wire-like) push–pull compounds, only relatively recently have analogous systems with two-dimensional conjugation[1,2] begun to attract attention. Accordingly, compounds have been reported with multiple donor and acceptor groups and multiple conjugated paths between them.[3−7] The two-dimensional nature of these structures is integral to their design and resultant properties. For example, spatial separation of the frontier orbitals in cruciform structures gives rise to particularly useful photophysical properties for sensing.[6]

Of course, there are many possible fundamental configurations of two-dimensional π-systems. We recently reported the synthesis and characterization of a set of "push–pull macrocycles", **D(mP)$_2$A** and **D(Th)$_2$A**, which feature electron-rich and -poor units linked by two conjugated bridges.[8−10] Pairing of the bridges was found to have a large effect on the photophysical properties of the compounds when compared to acyclic analogs **D(mP)A** and **D(Th)A**. Notably, the rate of radiative charge recombination for the linearly conjugated 2,5-thiophene-based system was dramatically reduced, an effect we attributed to a reduction in electronic coupling because of the symmetry of the macrocycle.[11,12]

Here, we report a new set of macrocycles with both 2,5-thiophene and *m*-phenylene bridges. Included in this series is compound **D(mP/Th)A**, which allows us to explore the properties of chromophores with donor and acceptor groups linked by different bridges with very different behavior: the 2,5-thiophene bridge is linearly conjugated, and the *m*-phenylene bridge is cross-conjugated.[13] Taken separately, charge transfer mediated by the linearly conjugated bridge should be efficient, whereas cross-conjugated moieties are

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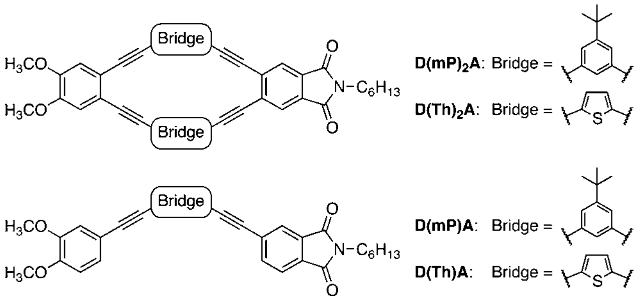
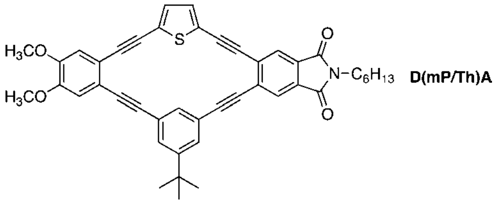
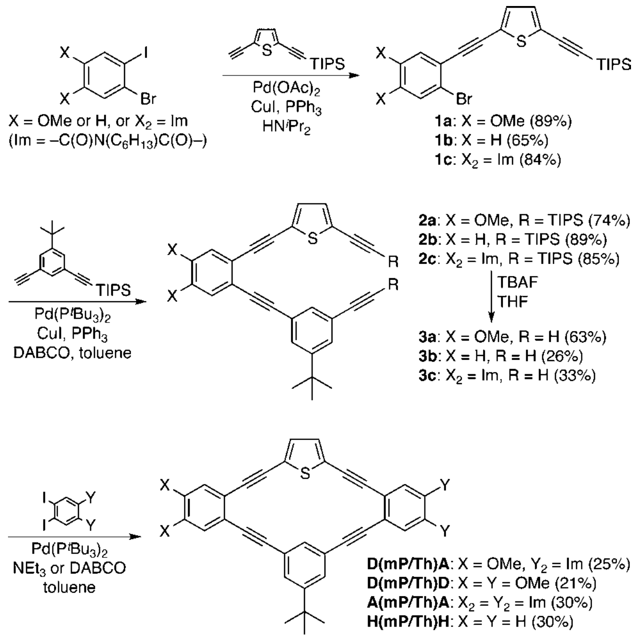


known to facilitate charge transfer but hinder recombination;[14,15] cross-conjugated systems have also been proposed as the basis for single-molecule transistors.[16,17] This push–pull macrocycle allows us to address whether one bridge dominates the photophysical properties (i.e., whether the properties are predicted by acyclic analogs such as **D(Th)A**) or whether these multiple conjugation paths can only be understood as a combined unit. The control over excited-state properties and charge-transfer rates afforded by this two-dimensional π-system design may ultimately have applications in photovoltaics and single-molecule devices.



Scheme 1



To the best of our knowledge, macrocycles with this combination of 2,5-thiophene and *m*-phenylene units are unknown. The synthesis of push–pull, donor–donor, acceptor–acceptor, and unsubstituted compounds **D(mP/Th)A**, **D(mP/Th)D**, **A(mP/Th)A**, and **H(mP/Th)H** is a straightforward modification of the synthetic strategy we used for our original series of macrocycles,[8] as shown in Scheme 1. Beginning with 1-bromo-2-iodoarenes, Sonogashira coupling was used to add first the 2,5-thiophene bridges followed by the *m*-phenylene bridges, giving compounds **1** and then **2** in good yields. The *tert*-butyl groups were included on the *m*-phenylene units to ensure good solubility and hinder aggregation, which would complicate spectroscopic characterization. Unfortunately, deprotection of the TIPS groups to give compounds **3** gave only modest isolated yields. Although this is typically a highly efficient reaction, we observed decomposition to unidentified byproducts; further, chromatographic isolation of the target compounds from nearly coeluting impurities required us to sacrifice yield for purity. The key macrocyclization step using copper-free Sonogashira coupling conditions with $Pd(P^tBu_3)_2$ as the catalyst[18] gave the target compounds in modest but workable yields, similar to those previously obtained for bis(2,5-thiophene) macrocycles (e.g., 34% for **D(Th)$_2$A**). These low yields are readily explained by the relatively poor fit of the 2,5-thiophene unit within the macrocyclic framework (see below).

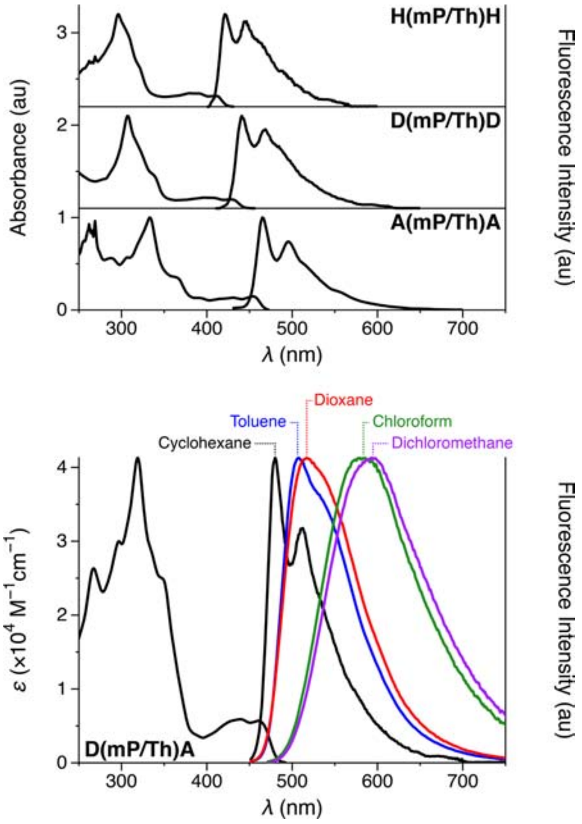


Figure 1. UV–vis (left) and fluorescence (right) spectra of **H(mP/Th)H**, **D(mP/Th)D**, and **A(mP/Th)A** (top) and of **D(mP/Th)A** (bottom). The spectra correspond to cyclohexane solutions except for the fluorescence spectra of **D(mP/Th)A**.

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UV−vis and fluorescence spectra of the macrocycles are shown in Figure 1. In all cases, the shapes of the spectra are independent of concentration (10^{-5}−10^{-7} M), suggesting that ground-state aggregation of the macrocycles is insignificant under these conditions and that emission does not occur from excimer states. The shapes of the UV−vis and fluorescence spectra of the symmetrical macrocycles **H(mP/Th)H**, **D(mP/Th)D**, and **A(mP/Th)A** show little dependence on solvent polarity (see Figure S1). The UV−vis spectra of **D(mP/Th)A** are also solvent-independent (see Figure S2), suggesting that excitation of this push−pull compound occurs to a locally excited state even in polar media. In contrast, its fluorescence spectra red shift with increasing solvent polarity, with the loss of vibronic structure, suggesting that emission occurs from a charge-transfer state in polar solvents. Fluorescence properties of the macrocycles are compiled in Table 1; data for the previously reported **D(Th)$_2$A** and **D(Th)A** are included for comparison.[8] In general, the mixed-bridge macrocycles are highly fluorescent ($\Phi_f \approx 0.2$). The excited-state dipole moment of the charge-transfer state of **D(mP/Th)A** (μ_e = 34 D) was estimated by Lippert−Mataga analysis of the fluorescence solvatochromism, as described in the Supporting Information. Fluorescence lifetimes (τ_f) were measured by time-correlated single photon counting which gave good monoexponential fits in all cases. Radiative (k_r) and nonradiative (k_{nr}) rate constants were calculated from Φ_f and τ_r ($k_r = \Phi_f\tau_f^{-1}$, $k_{nr} = (1 - \Phi_f)\tau_f^{-1}$).

Table 1. Excited-State Dipole Moments, Quantum Yields, Fluorescence Lifetimes, and Radiative and Nonradiative Rate Constants

	μ_e (D)	solvent[a]	Φ_f	τ_f (ns)	k_r ($\times 10^8$ s^{-1})	k_{nr} ($\times 10^8$ s^{-1})
D(mP/Th)A	34	Cy	0.18	1.61	1.1	5.1
		Diox	0.21	1.74	1.2	4.5
		CH_2Cl_2	0.18	2.87	0.63	2.9
D(mP/Th)D		Cy	0.26	1.16	2.2	6.4
A(mP/Th)A		Cy	0.24	1.53	1.6	5.0
H(mP/Th)H		Cy	0.20	0.91	2.2	8.8
D(Th)$_2$A[b]	25	CH_2Cl_2	0.005	1.0[c]	0.05	10
D(Th)A[b]	33	CH_2Cl_2	0.11	0.62	1.8	14

[a] Cy = cyclohexane, Diox = 1,4-dioxane. [b] Data from ref 8. [c] Average lifetime from a double exponential fit.

The effect of the two bridges on the photophysical properties can be understood by considering the electronic structures of the compounds, which were explored by DFT calculations. Simplified versions of each macrocycle were considered, with hexyl and *tert*-butyl groups replaced with hydrogen atoms (giving **D(mP/Th)A′**, etc.). The geometries were optimized at the B3LYP/6-31+G(d,p) level and are shown in Figures 2 and S3. The rather shallow angle of the 2,5-thiophendiyl moiety (~140°) is not well-accommodated within the macrocyclic framework. Consequently, intraannular steric interactions lead to a ~23°−25° twist of thiophene rings from the planes of the macrocycles; this out-of-plane twist is about half that previously determined for **D(Th)$_2$A** at the same level of theory (~42°). In contrast, the *m*-phenylene unit is very close to coplanarity with the macrocycle.

To model the spectroscopic properties, the optimized geometries were further probed by TD-DFT using the CAM-B3LYP functional,[19] which should better handle charge-transfer states[20] (see FMOs in Figures 2 and S3). Key calculated properties of all compounds are summarized in Table 2, and predicted spectra are shown in Figure S4. The variation in the energies of the first excited states, extracted from the low-energy absorption bands of the UV−vis spectra, are well-reproduced by the calculations, with a slight overestimation of ~0.1 eV in each case. The shifts in the spectra of the symmetrical compounds, **H(mP/Th)H**, **D(mP/Th)D**, and **A(mP/Th)A** (Figure 1, top), are easily explained by their HOMO−LUMO gaps, as shown in Figure S5.

As expected, for the push−pull compound **D(mP/Th)A′** the electron-rich veratrole moiety is the principal contributor to the HOMO, whereas the electron-deficient phthalimide moiety is the principal contributor to the LUMO. Delocalization through the linearly conjugated thiophene bridge is more pronounced than through the cross-conjugated *m*-phenylene bridge. The lowest energy transition of **D(mP/Th)A′** is predicted to be primarily a direct HOMO−LUMO transition (60% contribution), corresponding to a net change in dipole of $\Delta\mu$ = 8.40 D. This value is much smaller than that estimated by Lippert−Mataga analysis of the experimental fluorescence spectra and is consistent with the minimal solvatochromism observed in the UV−vis spectra.

The behavior of this new push−pull macrocycle **D(mP/Th)A** is perhaps best considered in the context of the previously reported acyclic and symmetrically bridged analogs **D(Th)A** and **D(Th)$_2$A**. Direct comparisons of the UV−vis and fluorescence spectra of **D(mP/Th)A** with these other compounds are given in the Supporting Information (Figure S6). Because *m*-phenylenes are often considered to "break" conjugation,[21] one might expect the photophysical properties of this push−pull macrocycle to closely resemble those of the acyclic, thiophene-bridged compound **D(Th)A**, with the cross-conjugated *m*-phenylene bridge acting primarily as a passive structural unit analogous to a nonconjugated linker. Indeed, the fluorescence spectra of **D(mP/Th)A** are a good match to those of **D(Th)A**; further, Lippert−Mataga analysis yields virtually identical excited state dipole moments, and their fluorescence quantum yields are similar.

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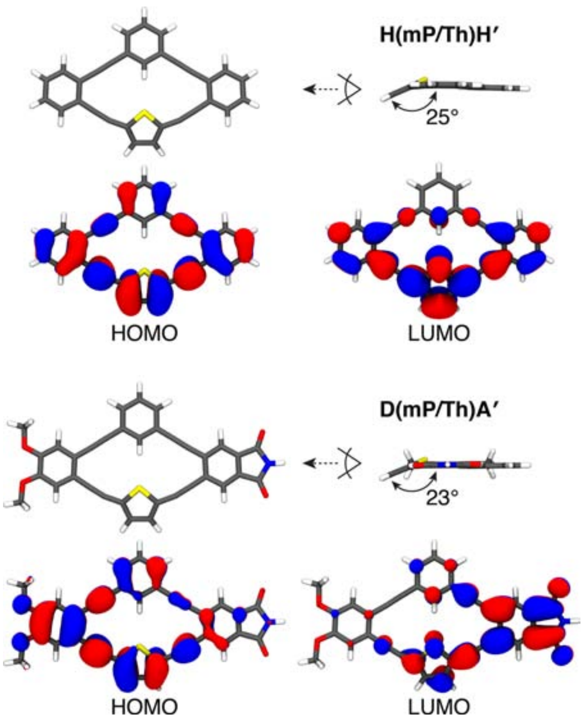

Figure 2. Optimized geometries of **H(mP/Th)H′** and **D(mP/Th)A′** (PCM(cyclohexane)/B3LYP/6-31+G(d,p)), viewed from above (top left) and from along the molecular long axis (top right), and representations of the frontier molecular orbitals (PCM/CAM-B3LYP/6-311+G(2d,2p)//PCM/B3LYP/6-31+G(d,p)).

Table 2. HOMO/LUMO Levels, First-Excited State Energies and Compositions, and Experimental First Excitation Energies

	HOMO (eV)	LUMO (eV)	$\Delta E_{\mathrm{H-L}}$ (eV)	$S_0 \rightarrow S_1$ energy (eV) [composition][a]	exptl (eV)
H(mP/Th)H′	−6.85	−1.41	5.44	3.10 [H → L (88%)]	3.02
D(mP/Th)D′	−6.46	−1.21	5.25	2.99 [H → L (85%)]	2.90
A(mP/Th)A′	−7.28	−2.32	4.96	2.82 [H → L (83%)]	2.73
D(mP/Th)A′	−6.76	−2.06	4.70	2.81 [H → L (60%)]	2.69

[a] H = HOMO, L = LUMO.

However, in contrast to these fluorescence properties, the UV−vis spectra of **D(mP/Th)A** are a much better match to those of macrocycle **D(Th)$_2$A**. In particular, they share a weak low energy transition above 450 nm ($\varepsilon \approx 5000\ \mathrm{M^{-1}\,cm^{-1}}$). The lower energy of this HOMO−LUMO absorption in the macrocycles appears to be due to the stabilization of the LUMO through extension of the conjugation into the second bridge, irrespective of its precise structure. We originally rationalized the weak intensity of this band for macrocycle **D(Th)$_2$A** by noting that the direct charge-transfer transition is symmetry forbidden. Clearly, this is not the case for **D(mP/Th)A**, which is not a symmetrical compound. However, the TD-DFT calculations do predict that the oscillator strength for the transition to the first excited state of **D(mP/Th)A′** (f = 0.32) is much closer to that of **D(Th)$_2$A′** (f = 0.00) than that of **D(Th)A′** (f = 1.86). This similarity can be understood by the observation that the HOMO and LUMO of **D(mP/Th)A′** remain approximately symmetric and antisymmetric with respect to the axis of charge transfer (Figure 2), despite the structural differences between the two bridges.

This effect extends to the fluorescence properties as well. Consider **D(mP/Th)A** and **D(Th)A** in CH$_2$Cl$_2$: the fluorescence quantum yields are similar; however, the lifetime of the charge transfer state of the mixed-bridge macrocycle is roughly 5-fold longer, corresponding to a 3-fold decrease in the radiative rate constant (k_r) and a 5-fold decrease in the nonradiative rate constant (k_nr). The decrease in k_nr is likely due to reduced vibrational deactivation because of the structural rigidity provided by the second bridge. The decrease in k_r is substantial, but not as significant as the 22-fold decrease observed for **D(Th)$_2$A**. Assuming that the frontier MOs in the relaxed charge-transfer state are similar to those in Figure 2, the relative k_r values can be explained by the relative strengths of the HOMO−LUMO transitions as discussed above.

The two-dimensional π-systems of these mixed-bridge compounds are clearly complex, as analogous acyclic or symmetrical macrocyclic compounds fail to predict their behavior. The effect on the rate of radiative charge transfer suggests that this mixed-bridge structural motif may ultimately offer a means to tune the electronic coupling, a key parameter in determining the lifetimes of charge-transfer states[22] and in the construction of single-molecule devices.[23]

In summary, we have prepared the first examples of a set of shape-persistent macrocycles with both 2,5-thiophene and *m*-phenylene moieties. The compounds with symmetrical substitution patterns are highly fluorescent ($\Phi_\mathrm{f} \approx 0.2$), with similar UV−vis and fluorescence spectra that systematically shift according to substituent effects on their HOMO−LUMO gaps. Excitation of the push−pull compound yields a charge-transfer state with properties intermediate between those of the acyclic and symmetrical macrocyclic thiophene-bridged analogs.

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Supporting Information Available. Supplemental figures, experimental details and procedures, NMR spectra of synthesized compounds, and Cartesian coordinates of optimized geometries. This information is available free of charge via the Internet at http://pubs.acs.org.

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