

## Mixed-valent molecular triple-deckers

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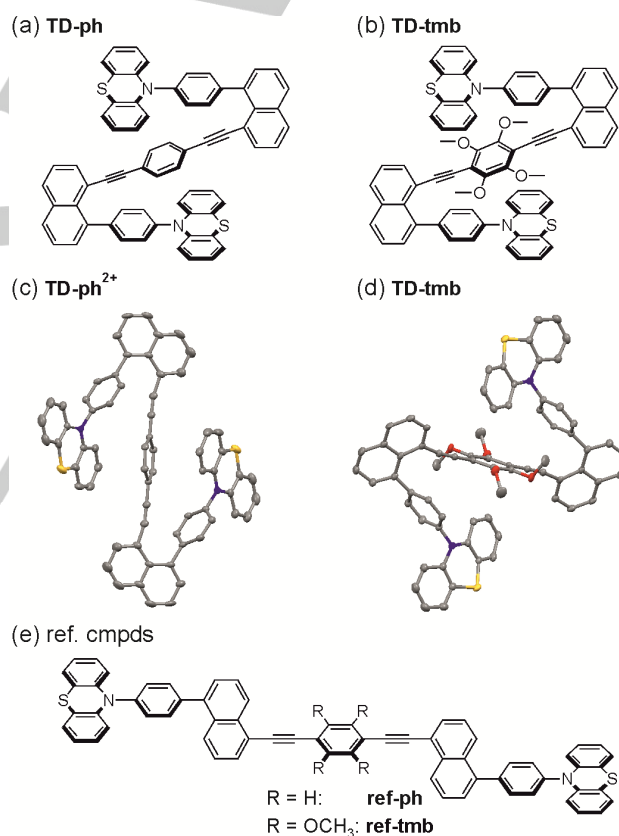
Dedicated to Professor Dietmar Stalke on the occasion of his 60<sup>th</sup> birthday

**Abstract:** Two phenothiazine (PTZ) moieties were connected via naphthalene spacers to a central arene to result in stacked PTZ-arene-PTZ structure elements. Benzene and tetramethoxybenzene units served as central arenes mediating electronic communication between the two PTZ units. Based on cyclic voltammetry, UV-Vis-NIR absorption, EPR spectroscopy, and computational studies, the one-electron oxidized forms of the resulting compounds behave as class II organic mixed-valence species in which the unpaired electron is partially delocalized over both PTZ units. The barrier for intramolecular electron transfer depends on the nature of the central arene sandwiched between the two PTZ moieties. These are the first examples of rigid organic mixed-valent triple-decker compounds with possible electron transfer pathways directly across a stacked structure, and they illustrate the potential of oligo-naphthalene building blocks for long-range electron transfer and a future molecular electronics technology.

Electron transfer (ET) has been studied in many donor-acceptor compounds with numerous types of molecular bridges. Whilst  $\pi$ -conjugation in such systems is important, ET usually proceeds along  $\sigma$ -bonded pathways even in the most efficient human-made molecular wires known to date.<sup>[1]</sup> Investigations of ET across  $\pi$ -stacks in structurally well-defined artificial compounds are far less common,<sup>[2]</sup> presumably because it is challenging to control  $\pi$ -stacking by synthetic means in small molecules. Work on mixed-valence systems with paracyclophane bridging elements showed that ET pathways directly across stacks can be important,<sup>[3]</sup> but artificial ET systems with more than two  $\pi$ -conjugated units stacked on top of each other require very careful molecular design.<sup>[4]</sup> Whilst numerous prior studies investigated charge transfer pathways involving through-space interactions,<sup>[5]</sup> the compact and comparatively rigid structures of our triple-decker compounds are very unusual. Moreover, oligo-naphthalenes are an underexplored type of molecular bridges and wires (particularly when compared to oligo-*p*-phenylenes), and our study showcases the potential of this class of linkers for charge transfer across a range of different pathways.

We hypothesized that by using 1,8-disubstituted naphthalene as a key structural element, rigid symmetrical compounds comprised of a central arene ring with (more or less) planar redox-active units at relatively short distance above and below that arene ring would be accessible. We chose phenothiazine

(PTZ) as redox-active moieties and a simple unsubstituted phenyl (ph) ring (Fig. 1a) or a tetramethoxybenzene (tmb) unit as a central arene (Fig. 1b), anticipating that one-electron oxidation of a single PTZ would lead to mixed-valent compounds in which intramolecular ET across the stacked structure (or possibly through space) could be probed. We also attempted to synthesize and to explore isomeric reference compounds in which the naphthalenes are substituted at their 1- and 5-positions (Fig. 1e). There have been many studies of organic mixed-valence compounds,<sup>[6]</sup> but we are unaware of prior investigations of such rigid molecular triple-deckers (TDs).



**Fig. 1.** (a, b) Molecular structures of the two main compounds; (c, d) X-ray crystallographic structures of **TD-ph**<sup>2+</sup> (SbCl<sub>6</sub><sup>-</sup> anions not shown) and **TD-tmb** with thermal ellipsoids at the 50% probability level, H-atoms not shown. (e, f) Molecular structures of two reference isomers.

The two key compounds **TD-ph** and **TD-tmb** were synthesized and characterized as described in the Supporting Information (SI, pages S2-S12). By slow diffusion of pentane into CH<sub>2</sub>Cl<sub>2</sub> solutions, the doubly oxidized form of **TD-ph** as a SbCl<sub>6</sub><sup>-</sup> salt (Fig. 1c) as well as the charge-neutral form of **TD-tmb** (Fig. 1d) could be crystallized. In **TD-ph**<sup>2+</sup> the central phenyl ring has a roughly parallel orientation to an arene entity of each PTZ unit, with

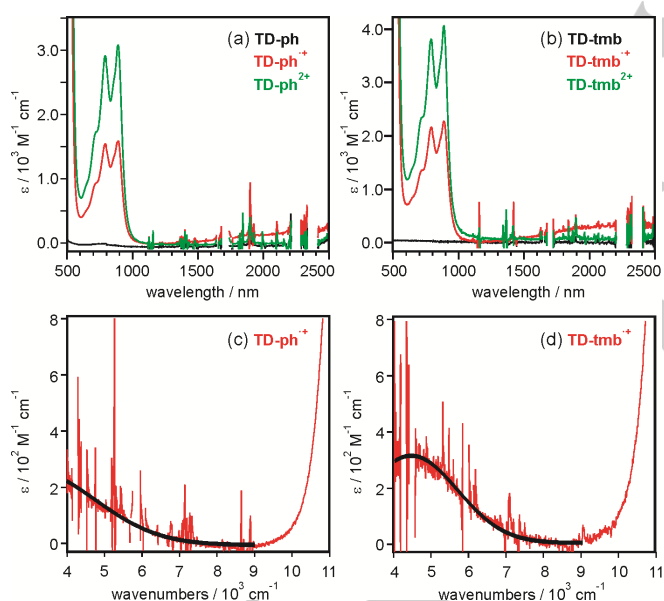
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distances of 3.92 and 3.96 Å between centroids of the respective ring planes. In **TD-tmb** such alignment is not present because of the steric demand of the methoxy-substituents (see SI page S13 for crystallographic details). For the mixed-valence forms direct structural information from X-ray diffraction could not be obtained due to lack of crystals, but computational studies provided further insight in these cases (see below). The reference compounds **ref-ph** and **ref-tmb** (Fig. 1e) were extremely poorly soluble in essentially all common solvents. In the case of **ref-ph** this precluded proper purification by chromatography, and therefore only **ref-tmb** could be fully characterized. However, neither of the two reference compounds was sufficiently soluble for electrochemical and spectroscopic studies, and consequently we were forced to focus exclusively on **TD-ph** and **TD-tmb**.

Cyclic voltammetry of **TD-ph** and **TD-tmb** in  $\text{CH}_2\text{Cl}_2$  with 0.1 M TBAPF<sub>6</sub> as supporting electrolyte leads to oxidation waves at 0.72 V vs. SCE in both cases, due to simultaneous one-electron oxidation of both PTZ units at very similar potential (Fig. S1, SI page S14). This may simply reflect the relatively weak electrostatic interaction between PTZ units across the central arene, because potential splittings in mixed-valence compounds are often dominated by electrostatic effects.<sup>[7]</sup> The comproportionation constants ( $K_c$ ) are 8 (**TD-ph**) and 9 (**TD-tmb**), see SI page S18.



**Fig. 2.** (a, b) Optical absorption spectra recorded in  $\text{CH}_2\text{Cl}_2$  at 22 °C. Black traces: before addition of chemical oxidant (charge-neutral forms). Red traces: mixed-valent monocationic forms. Green traces: dicationic forms. (c, d) IVCT absorption bands (red traces) and Gaussian fits (black traces). See SI pages S16-S18 for determination of extinction coefficients and in-depth analysis of titration data.

Intervalence charge transfer (IVCT) absorption bands are usually more diagnostic for mixed-valence compounds with significant electronic communication between individual redox centers, and therefore we focused on UV-Vis-NIR absorption studies of **TD-ph** and **TD-tmb** in  $\text{CH}_2\text{Cl}_2$ . In their charge-neutral

forms, both triple-deckers do not exhibit any significant electronic absorption at wavelengths longer than 500 nm (black traces in Fig. 2a/b). Following oxidation to the mixed-valent monocationic forms with  $\text{SbCl}_5$ , prominent absorption bands due to PTZ<sup>+</sup>-localized  $\pi$ - $\pi^*$  transitions emerge at 890, 790 nm and 510 nm (red traces). (The extinction coefficients of these bands are known,<sup>[8]</sup> and this fact was exploited to verify that proper amounts of oxidation equivalents were added). Furthermore, broad and comparatively weak NIR absorptions (1200 – 2500 nm) become detectable in both compounds, and upon further oxidation to the dicationic species these NIR absorptions vanish again (green traces in Fig. 2a/b), whilst the abovementioned PTZ<sup>+</sup>-localized  $\pi$ - $\pi^*$  transitions gain further in intensity. Evidently the NIR features between 1200 and 2500 nm only appear in the mixed-valent monocationic forms and are therefore attributed to IVCT absorption bands. Vibrational overtones of the solvent as well as atmospheric  $\text{CO}_2$  and  $\text{H}_2\text{O}$  interfere with the weak IVCT absorptions, leading to comparatively low signal-to-noise ratios and some gaps in the NIR absorption spectra.

**Table 1.** Through-space N-N distance ( $R_{AB}$ ), energy of the IVCT absorption band maximum ( $\nu_{\text{max}}$ ) corresponding to the reorganization energy ( $\lambda$ ), electronic coupling between PTZ moieties ( $H_{AB}$ ), and energy barrier for thermal ET ( $E_{\text{th}}$ ).

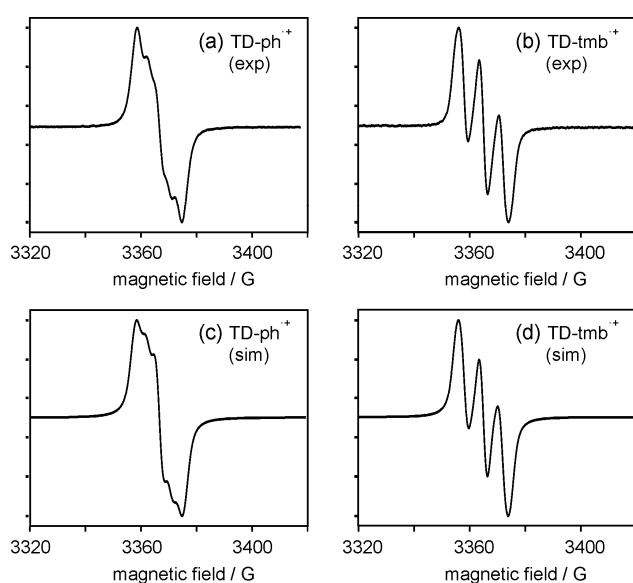
cmpd	$R_{AB} / \text{\AA}$	$\nu_{\text{max}} (= \lambda) / \text{cm}^{-1}$	$H_{AB} / \text{cm}^{-1}$	$E_{\text{th}} / \text{cm}^{-1}$
<b>TD-ph<sup>+</sup></b>	11.3	3030	~110	~650
<b>TD-tmb<sup>+</sup></b>	11.9	4430	~110	~1000

The IVCT bands can be fitted to single Gaussian functions (Fig. 2c/d), and analysis with Marcus-Hush theory permits estimation of the electronic coupling ( $H_{AB}$ ) between individual redox-active units (SI pages S18-S19).<sup>[9]</sup> On the basis of computed N-N distances (SI page S25) of 11.3 Å (**TD-ph<sup>+</sup>**) and 11.9 Å (**TD-tmb<sup>+</sup>**),  $H_{AB}$  values of ca. 110  $\text{cm}^{-1}$  are estimated for both triple-deckers (Table 1). In classical mixed-valence compounds with through-bond charge transfer pathways the effective ET distance can be considerably shorter than the geometrical distance between (formal) redox centers, but for our stacked compounds with their unusual three-dimensional structure it seems more reasonable to use the through-space N-N distance. The  $H_{AB}$  values found here are relatively large when considering that 23  $\sigma$ -bonds are between the two N-atoms.  $H_{AB}$  values on the order of 100  $\text{cm}^{-1}$  are more typically found for organic mixed-valence compounds with significantly shorter  $\sigma$ -bond pathways,<sup>[6a, 6b, 10]</sup> suggesting that a mixture of through-bond and through-space interactions is important in our triple-deckers. Unfortunately, solubility issues precluded investigation of the solvent-dependence of the IVCT absorptions.

In the class II mixed-valence regime the reorganization energy ( $\lambda$ ) is equal to the energy of the IVCT absorption band maximum ( $\nu_{\text{max}}$ ).<sup>[11]</sup> Using the values for  $\lambda$  and  $H_{AB}$  of **TD-ph<sup>+</sup>** and **TD-tmb<sup>+</sup>** from Table 1, the energy barriers for thermal ET ( $E_{\text{th}}$ ) can be estimated with eq. 1.<sup>[11a]</sup>

$$E_{\text{th}} = \lambda / 4 - H_{AB} + H_{AB}^2 / \lambda \quad (\text{eq. 1})$$

Whilst this represents a crude approximation, the qualitatively important finding is that the barrier for thermal ET is substantially higher for **TD-tmb**<sup>+</sup> than for **TD-ph**<sup>+</sup> (1000 vs. 650 cm<sup>-1</sup>, Table 1). This is in line with the EPR experiments discussed below. DFT calculations (SI page S24) indicate that the steric demand of the methoxy-substituents causes substantially larger dihedral angles between individual arene planes in **TD-tmb**<sup>+</sup> relative to **TD-ph**<sup>+</sup> (Fig. S11). The effect of steric congestion is also seen in the X-ray crystal structures of Fig. 1c/d, although the respective structures do not represent those of the mixed-valence forms. In the structure of **PTZ-ph**<sup>2+</sup> (Fig. 1c) one arene ring of each PTZ unit flanks the central benzene moiety with centroid-centroid distances of 3.92 and 3.96 Å, respectively, whilst in **PTZ-tmb** (Fig. 1d) the respective distances are considerably greater (4.80 Å) and the extent of co-planarity is much lower. Thus, steric effects are likely to make charge transfer pathways involving stacking and through-space interactions considerably less efficient in **TD-tmb**<sup>+</sup>.



**Fig. 3.** (a, b) Experimental X-band EPR spectra measured in CH<sub>2</sub>Cl<sub>2</sub> at 20 °C along with their simulations (c, d), yielding the EPR parameters in Table 2.

The EPR spectrum of **TD-ph**<sup>+</sup> in CH<sub>2</sub>Cl<sub>2</sub> (Fig. 3a) is compatible with delocalization of the unpaired electron over both PTZ units. The observable quintet ( $g = 2.0068$ ) is caused by the interaction of the electron spin with two equivalent nitrogen nuclei ( $a_N = 3.5$  G, Table 2) and different sets of protons ( $a_{H1} = 1.0$  G,  $a_{H2} = 0.8$  G,  $a_{H3} = 0.4$  G). Simulation of the experimental EPR data on the basis of DFT calculations (SI pages S20-S21, S24-S26) reveals the presence of a minority paramagnetic species (ca. 15%) interacting with only one nitrogen atom ( $a_N = 5.8$  G) and two sets of 2 equivalent protons ( $a_{H1} = 2.1$  G,  $a_{H2} = 1.1$  G). Taking that latter species into account, the simulated spectrum in Fig. 3c was obtained.

The X-band EPR spectrum of **TD-tmb**<sup>+</sup> in CH<sub>2</sub>Cl<sub>2</sub> is essentially a triplet (Fig. 3b,  $g = 2.0063$ ) caused by interaction of the unpaired electron with a single N-atom ( $a_N = 6.7$  G, Table 2), two pairs of

equivalent protons in closer proximity to the N-atom ( $a_{H1} = 2.1$  G,  $a_{H2} = 0.9$  G), and one set of four peripheral protons ( $a_{H3} = 0.3$  G) (SI page S21). This EPR signal is characteristic for the mononuclear PTZ radical,<sup>[8]</sup> suggesting that in **TD-tmb**<sup>+</sup> the unpaired electron is not delocalized over two PTZ units on the EPR timescale at 20 °C. However, the simulation of the experimental EPR spectrum (Fig. 3d) required the contribution (ca. 24%) of a second paramagnetic species in which the unpaired electron interacts with two equivalent <sup>14</sup>N nuclei ( $a_N = 3.5$  G), and two sets of 4 equivalent protons ( $a_{H1} = 1.0$  G,  $a_{H2} = 0.7$  G). Thus, the EPR spectra of **TD-ph**<sup>+</sup> and **TD-tmb**<sup>+</sup> both contain a contribution from delocalized and localized species. Whilst the delocalized species is dominant in **TD-ph**<sup>+</sup>, the localized species is more important in **TD-tmb**<sup>+</sup>. The different extents of delocalization found by EPR (Table 2) are in excellent agreement with the difference in barrier heights for thermal ET ( $E_{th}$ ) obtained from UV-Vis-NIR data analysis (eq. 1, Table 1). Specifically, thermal intramolecular ET at 298 K is estimated to be 5-7 times faster in **TD-ph**<sup>+</sup> than in **TD-tmb**<sup>+</sup> based on the two independent methods and data sets (SI pages S22-S23). Conformational degrees of freedom in our systems are somewhat more restricted than in other, sterically less congested and rigid mixed-valence compounds,<sup>[12]</sup> yet it is possible that conformational effects play a non-negligible role in leading to the different extents of delocalization.

**Table 2.** EPR parameters (relative contributions of signals and hyperfine coupling constants).

cmpd	contr.	$a_N$ / G	$a_{H1}$ / G	$a_{H2}$ / G	$a_{H3}$ / G
<b>TD-ph</b> <sup>+</sup>	85%	3.5 (2N)	1.0 (4H)	0.8 (4H)	0.4 (4H)
	15%	5.8 (1N)	2.1 (2H)	1.1 (2H)	
<b>TD-tmb</b> <sup>+</sup>	24%	3.5 (2N)	1.0 (4H)	0.7 (4H)	
	76%	6.7 (1N)	2.1 (2H)	0.9 (2H)	0.3 (4H)

In summary, we have reported on two structurally novel triple-decker compounds that behave as organic mixed-valence species with partial delocalization of an unpaired electron. Their unusual three-dimensional structure likely plays an important role in mediating charge transfer between the two redox-active PTZ centers, particularly in view of the long through-bond distance involving 23  $\sigma$ -bonds between N-atoms. The 1,8-substitution pattern at the naphthalene bridging units employed here is expected to provide only weak through-bond electronic coupling,<sup>[2b, 13]</sup> and it seems plausible that the overall charge transfer pathway includes a mixture of through-bond and through-space interactions. Long-range ET across oligo-naphthalene structures is yet far less well explored than across oligo-*p*-phenylenes,<sup>[14]</sup> and the insights gained here point to uncommon phenomena that deserve further attention in future studies, particularly in view of recent advances in the synthesis of oligo-naphthalenes.<sup>[15]</sup> The comparatively rigid and sterically congested molecular structures resulting from the naphthalene bridges used herein are rather uncommon for ET systems, and they provide access to a multitude of charge transfer pathways including  $\sigma$ -,  $\pi$ - and through-space interactions. Multi-

dimensional ET thus seems readily possible in appropriately substituted oligo-naphthalene structures.

## Acknowledgements

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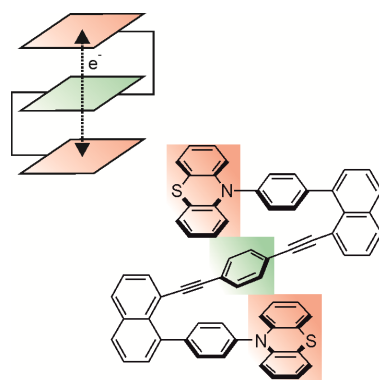
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## Entry for the Table of Contents

## COMMUNICATION

Through-bond and through-space charge transfer pathways are important in organic mixed-valence compounds with uncommon three-dimensional molecular structures based on naphthalene building blocks.



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