

Conductance Behavior of Tetraphenyl-Aza-BODIPYs

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ABSTRACT: We studied the electrical conductance of single-molecule junctions formed from molecular wires with 4 anchor groups. Three tetraphenyl-aza-BODIPYs with 4 or 2 thiomethyl anchor groups were synthesized and their single-molecule conductance measured using break-junction-STM. Using DFT based calculations these compounds were shown to contain a combination of constructive and destructive quantum interference, depending on the molecule's connectivity in the junction. A scissor correction is employed to obtain the corrected HOMO-LUMO gaps and a tight binding model (TBM) is used to highlight the role of quantum interference in the tetraphenyl-aza-BODIPY central unit.

Introduction

The field of single-molecule electronics contains many studies of linear pseudo- one-dimensional molecular wires with a single anchor group at each end.¹⁻³ Such systems have been crucial for the understanding and development of molecular conductance owing to their ability to be modified in a modular fashion. However, to incorporate greater functionality, there is a need to explore how electricity flows through molecular structures with multiple anchor groups. The challenge is that as additional anchor groups are added to a molecule, the number of potential conductance paths increases, thereby increasing the complexity of the analysis. An early study of such molecules was performed by Grunder *et al.*, whereby a 1,4-diethynyl-2,5-divinylbenzene motif was substituted by a combination of pyridyl and thiolate anchor groups, resulting in a system that could be electrochemically switched between conductive paths.⁴ A second experimental study examined the conductance of 2,11-dithia[3.3]paracyclophane, in which the combination of two parallel conductive paths resulted in a conductance of $9.7 \times 10^{-4} G_0$.⁵ This increase by a factor of 2.8 compared with the conductance of the equivalent single-path molecule, 1,4-bis[(methylthio)methyl]benzene ($3.5 \times 10^{-4} G_0$) was a consequence of constructive quantum interference (QI).⁵

In the present study we seek to examine a significantly different system to that of Grunder *et al.*;⁴ in which, rather than two conductive paths sharing a common conjugated core, two identical conductive parallel paths are held in close proximity, but are still linked by a conductive bridge. To realize such a structure, the tetraphenyl-difluoroboratriaza-indacene (tetraphenyl-aza-BODIPY) motif was chosen as it is a flat, rigid, highly conjugated molecule consisting of two 3,5-diaryl-substituted pyrrolates linked by a conjugated nitrogen and a BF_2^+ fragment (see Scheme 1). In addition to the low HOMO-LUMO energy gap, the 2,4-substitution pattern of the pyrrole has been shown by Yang to display destructive QI, while the 2,5-substituted analogue displayed none.⁶

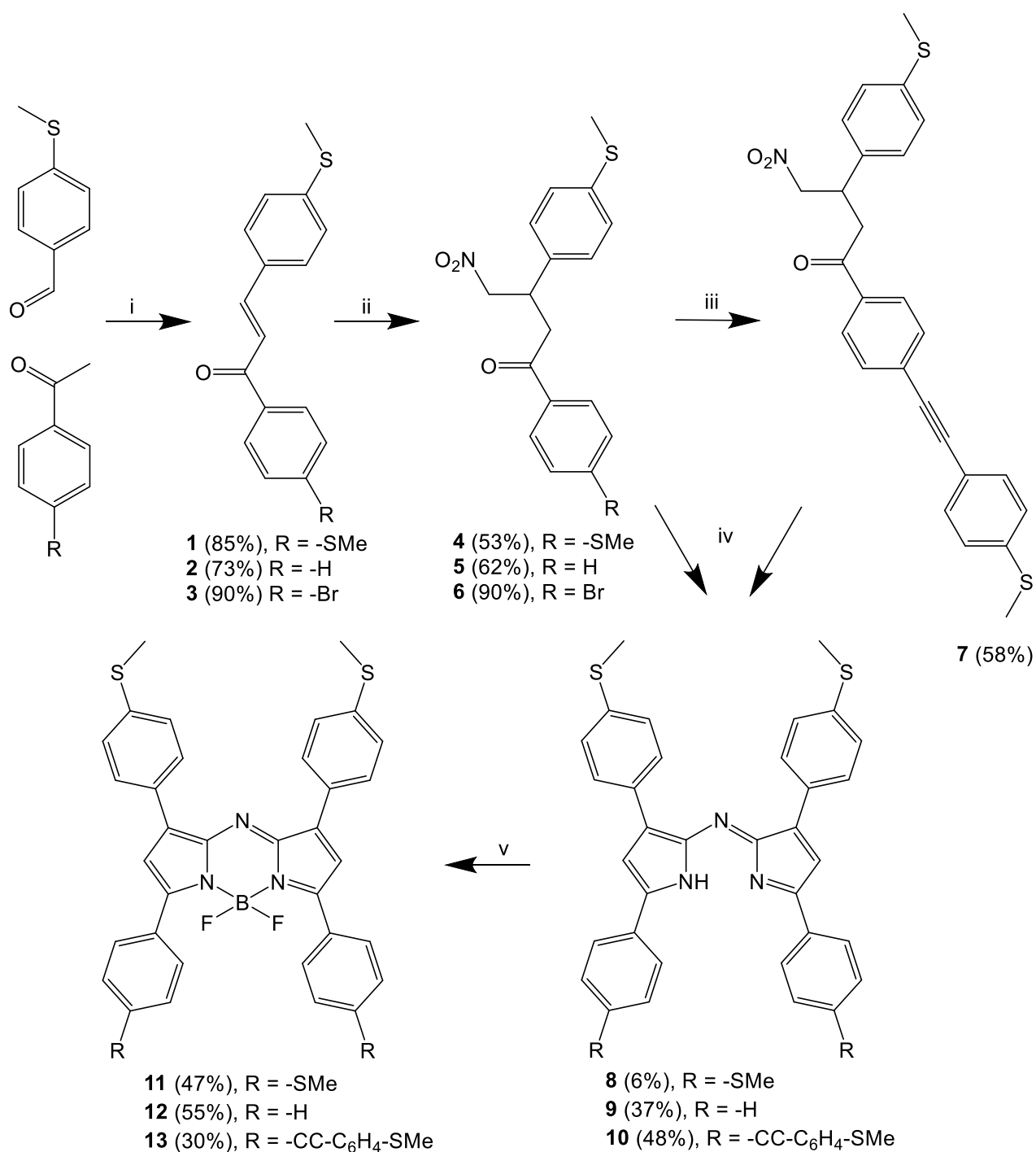
Since the aza-BODIPY motif was first reported by Sathyamoorthi et al. in 1993,⁷ these systems have been extensively studied due to their high near-infrared emission and biological stability,⁸⁻¹¹ which make them ideally suited as cellular stains. Furthermore, due to the work of O'Shea et al.,¹²⁻¹⁴ their synthesis has become readily accessible. This present work examines the electrical conductance of the aza-BODIPY substituted with para-thioanisole moieties to give terminal thiomethyl anchor groups. This particular moiety was chosen as its symmetry limits any DQI effects to the aza-BODIPY core and the thioether contacts are known to favor mid-gap conductance.¹⁵ For this motif, the HOMO is delocalized over the entire molecule whereas the LUMO is localized to the aza-BODIPY core.

Synthesis

The synthesis of target compounds **11** and **12** was according to O'Shea's procedure (see Scheme 1).¹³⁻¹⁴ Following the synthesis of the chalcones (**1-3**) from 4-(methylthio)benzaldehyde and the corresponding ketone (acetophenone, 1-(4-(methylthio)phenyl)ethan-1-one or 1-(4-bromophenyl)ethan-1-one) via an aldol reaction, nitromethane was added via Michael addition to give **4-6**. The formation of the aza-DIPY's (**8** and **9**) was achieved by heating **5** and **6** with ammonium acetate in n-butanol. Although significant quantities of the crude precipitate were obtained, Soxhlet extractions were necessary to achieve sufficiently pure samples, resulting in the lower yields of **6** (**8**) and 37% (**9**). Conversion to their BF₂-chelates, **11** and **12**, was achieved by stirring BF₃·OEt₂ with Et₃N and the corresponding aza-DPY (**8** and **9**).

Due to solubility limitations, the synthesis of **13** deviated from the established approach of Bouit et al. and Bellier et al.,¹⁶⁻¹⁷ instead using Daddario et al.'s method,¹⁸ performing a Sonogashira coupling on a bromo-substituted aza-DIPY precursor. Sonogashira coupling was

performed with 1-(4-bromophenyl)-3-(4-(methylthio)phenyl)-4-nitrobutan-1-one (**6**) and 4-ethynylthioanisole to give 3-(4-(methylthio)phenyl)-1-(4-((4-(methylthio)phenyl)ethynyl)phenyl)-4-nitrobutan-1-one (**7**); the synthesis then followed O'Shea's approach to give the corresponding aza-DIPY (**10**) and aza-BODIPY (**13**). All compounds were fully characterized by ^1H , ^{13}C and ^{19}F NMR spectroscopy, high resolution mass-spectrometry or elemental analysis.



Scheme 1. Synthesis of substituted aza-BODIPYs using i) NaOH, H₂O/EtOH, ii) MeNO₂, MeOH, Et₂NH, iii), 4-ethynylthioanisole, PdCl₂(PPh₃)₂, CuI, Et₃N, THF, iv) NH₄OAc, n-butanol, v), BF₃·OEt₂, Et₃N, DCM.

Molecular Structures

Structures of **4**, **6**, **11**, **12**, and **13** were confirmed by single-crystal X-ray diffraction and were consistent with the obtained spectroscopic data. The molecular structures of **11-13** are shown in Figure 1. The central tricyclic moieties in these compounds show surprising conformational versatility; while that of **11** is planar within 0.07 Å, in **12** and **13** the dihedral angles between the planes of the two pyrrolys (the folding angle along B...N line of the central cycles) are 24.3° and 22.1° respectively. Less surprising is a wide range of orientations of phenyl substituents, characterized by torsion angles around C(aza-BODPY)-C(Ph) bonds. In compounds **11-13** these angles vary from 12.6(8)° to 38.3(4)° for the distal (to the BF₂) phenyl-group in **11** and **12** respectively. These values are in a good agreement with those found in the structures of 3-unsubstituted 2,4-diphenyl pyrroles (29 entries in the CSD), where distal-phenyl groups are inclined to be co-planar with pyrrole rings (the absolute values of corresponding torsion angles are below 35°). The molecule of the only known 3,5-unsubstituted 2,4-phenylpyrrole is virtually planar.¹⁹

The introduction of the second parallel conductive paths in the molecules **11-13** results in two likely contact orientations: straight (along the path) and diagonal (via the central heterocycle) ones. The average values of S...S distances for these two types of contacts are ca. 13.6 and 16.2 Å for molecule **11** and 20.4 and 22.9 Å for compound **13** respectively. Similar average S...p-H distances in molecule **12** are 12.9 and 15.3 Å for straight and diagonal paths respectively.

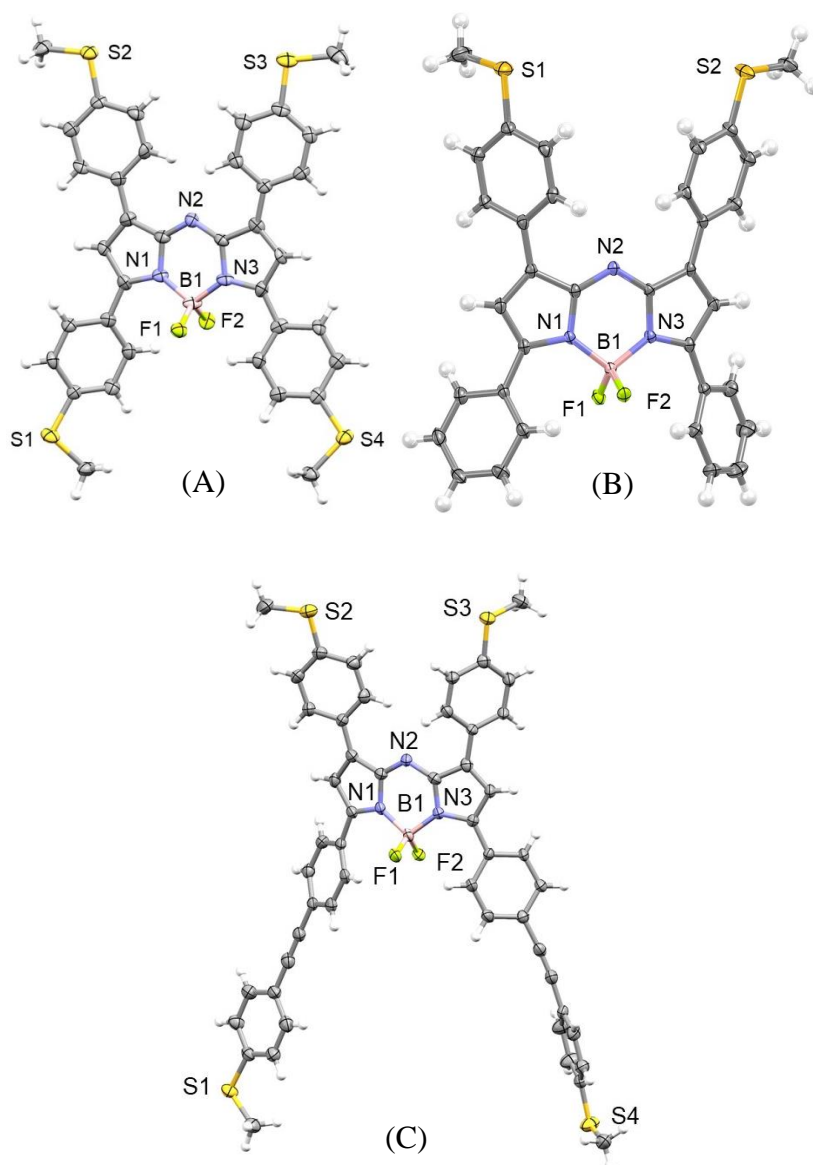


Figure 1. Crystal structures of **11** (A), **12** (B) and **13** (C), where the solvent molecule and disorder have been removed for clarity; thermal ellipsoids displayed at 50% probability.

Electrochemistry

The three new aza-BODIPYs (**11-13**) were characterized by cyclic and differential pulse voltammetry in DCM using a Fc/Fc^+ internal reference. Redox potentials and frontier orbital

energies are given in Table 1. Each of the compounds (**11-13** and tetraphenyl-aza-BODIPY) displayed two separate reductions, at very similar potentials for the four molecules (± 0.04 V for the 1st reduction and ± 0.08 V for the 2nd) suggesting little effect on the LUMO and LUMO+1 due to changes in distal (to the boron) phenyl group substitution. For compounds **11** and **13**, two separate oxidations were observed, while only a single oxidation was observed for **12**. Such a difference suggests that the electron donation of the thiomethyl causes destabilization of the HOMO. This is reflected in the series of aza-BODIPY **12** and **11**; as the number of thiomethyl groups increases, the oxidation potential decreases. In the case of **13**, despite the molecule containing four thiomethyl groups, the inclusion of the alkyne between the proximal (to the boron) phenyl group and the thioanisole stabilizes the HOMO. These results suggest that while modifying the molecules in this fashion will alter any conductance paths involving the HOMO, any LUMO dominated paths will be unchanged.

Table 1. Electrochemical data for aza-BODIPYs **11-13**

Compound	Oxidation Potential ($V_{Fc/Fc+}$)		Reduction Potential ($V_{Fc/Fc+}$)		HOMO (eV)	LUMO (eV)	LUMO+1 (eV)
	1 st	2 nd	1 st	2 nd			
tetraphenyl-aza-BODIPY ²⁰	0.90		-0.81	-1.61			
11	0.51	0.79 ^a	-0.85	-1.53	-5.374	-4.083	-3.390
12	0.73		-0.81	-1.58	-5.468	-4.028	-3.249
13	0.66	0.89 ^a	-0.77	-1.43	-5.477	-4.068	-3.389

^aIrreversible

Photochemistry

Aza-BODIPY compounds typically absorb and emit in the red to near-infrared region of the spectrum. Such low energy transitions are typically very sensitive to environmental effects, providing a means of modulating the energies of the frontier orbitals by varying the solvent. As such, the absorbance and emission spectra of the aza-BODIPYs (**11-13**) were recorded in

solvents with different polarities, DCM (ϵ_r , 8.93), THF (ϵ_r , 7.60), EtOAc (ϵ_r , 6.02), CHCl₃ (ϵ_r , 4.81), and toluene (ϵ_r , 2.38), with solubility preventing measurements in cyclohexane and acetonitrile.

Each of the complexes displayed a S₀→S₁ band at 600–800 nm with S₀→S₂ transition at 519–590 nm (see Figure 2);¹⁸ this is significantly red-shifted relative to the parent aza-BODIPY and the methoxy analogue ($\lambda_{\text{abs max}} = 691 \text{ nm}$).²¹ As the S₀→S₁ transition is purely HOMO→LUMO in character, a comparison can be made with the electrochemical data, showing approximately the same trend $\Delta E_{\text{echem}}|\text{HOMO-LUMO}| = \mathbf{11} < \mathbf{13} < \mathbf{12}$ and absorbance $\Delta E_{\text{abs}}|\text{HOMO-LUMO}| = \mathbf{13} \leq \mathbf{11} < \mathbf{12}$. Based on the electrochemical data, this is attributed to the electron donation of the thiomethyl group destabilizing the HOMO, with a limited effect on the LUMO. Given the S₀→S₁ transition offers a measure of the $\Delta E|\text{HOMO-LUMO}|$, this can be used to examine the effect of solvent polarity on the frontier orbital energy. Comparing the solvent range of DCM→CHCl₃ for **11**, $\Delta E = 0.012 \text{ eV}$ and for DCM→toluene, $\Delta E = 0.021 \text{ eV}$ for **12** and 0.014 eV for **13**, demonstrating a small but significant environmental effect on the frontier orbitals, if conductance were to occur via a sharp resonance near the Fermi energy such a variation in the $\Delta E|\text{HOMO-LUMO}|$ would likely result in a large change in conductance. In addition to the solvatochromic measurements, the photophysical measurements were completed with the determination of relative PLQYs and emission lifetimes, which were 0.32–0.71, significantly higher than that of similar ‘simple’ aza-BODIPYs; coupled with longer-than- usual emission lifetimes and red-shifted emissions (Table 2), this warrants further investigation.

Table 2. Photochemical data for aza-BODIPYs **11-13**

Compound	Absorption, nm ($\epsilon \times 10^3$, L mol ⁻¹ cm ⁻¹)	S ₁ -S ₀ , eV	Emission, nm	Lifetime, ns	PLQY
Aza-BOPY ²¹	468 (6.0), 647 (85)		682	0.78	0.30

11	717 (93), 536 (25), 367 (sh,19), 326 (28), 272 (55)	1.618	758	2.6	0.71
12	672 (92), 535 (sh, 21), 312 (43), 270 (41)	1.717	735	1.7	0.32
13	717 (79), 552 (23), 379 (sh, 25), 331 (59), 288 (42)	1.633	761	2.0	0.47

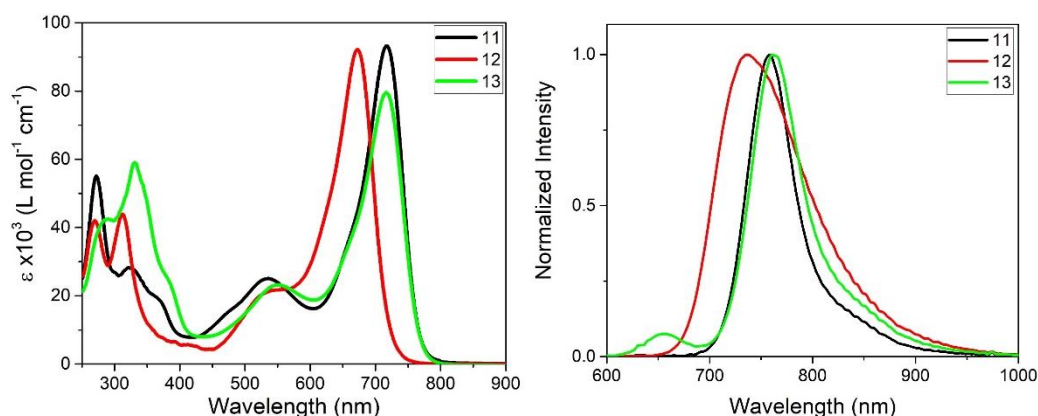


Figure 2. a) Absorption spectra of aza-BODPYs **11-13** recorded in DCM, and b) emission spectra of aza-BODPYs **11-13** recorded in DCM.

Conductance

The conductance of a series of compounds was measured using the BJ-STM technique and a THF/mesitylene solution (**11**, **12** and **13**), see Figure 3. Compounds **11** and **13** both show conductance peaks at $4.0 \times 10^{-4} G_0$ and $2.5 \times 10^{-5} G_0$ respectively. The lower conductance of **13** is consistent with the 0.6 nm increased length of **13**. The greater length of **13** is also reflected in an increased break-off distance, although the latter increase is less than the difference in molecular lengths, suggesting that the molecules may not be fully extended in the gold-molecule-gold junctions. This can be attributed to the stochastic nature of the junction breaking process, the fact that the thiomethyl group binds more weakly to gold than a thiol group and the degree of steric hindrance provided by the terminal methyl groups. As such, a distinction cannot be made between the contacts being made diagonally through the proximal and the distal phenyl rings and two pyrrole rings, or vertically through only the proximal and distal

phenyl rings and a single pyrrole ring. However, no conductance peak was evident for **12**, confirming that the conductance path does not pass through a proximal ring to the second proximal ring, therefore it is assumed that it cannot pass through both distal rings either. This is consistent with the break-off distance of both **11** and **13** being greater than the 0.7 nm S-S distance between either the distal or proximal pairs. Measurements were also performed in CHCl₃:air (depositing the compounds in CHCl₃ and measured in air), giving a lower hit rate but comparable conductance values of $2.1 \times 10^{-4} G_0$ (**11**) and $2.7 \times 10^{-5} G_0$ (**13**), with no conductance peak observed for **12**. Such variations in conductance with respect to solvent are common.²²

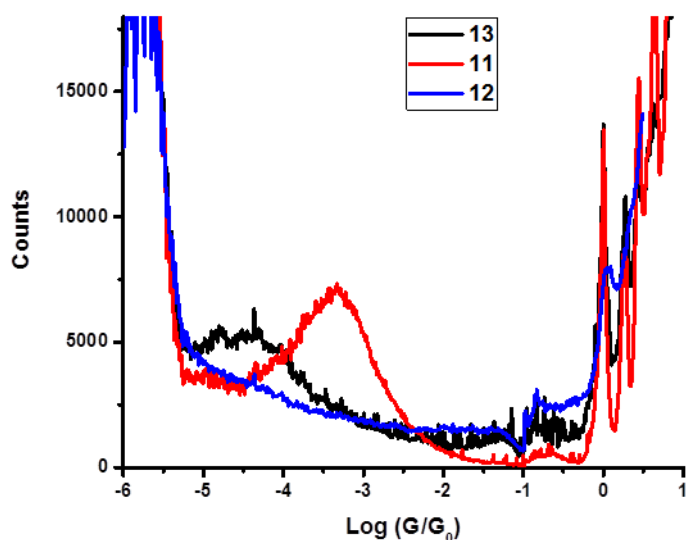


Figure 3. Conductance histograms of compounds **11-13** recorded in THF/Mesitylene

Table 3. Conductance values and break-off distances of compounds **11-13**

Molecule	Conductance (G/G_0)		Break-Off distance (nm)	
	THF/Mesitylene	CHCl ₃ /Air	THF/Mesitylene	CHCl ₃ /Air
11	4.0×10^{-4}	2.1×10^{-4}	1.4	1.4

13	2.5×10^{-5}	2.7×10^{-5}	1.6	1.6
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Theory

We started by modelling the binding between terminal groups and Au, and then relaxed each compound in the presence of fixed leads. Using the density functional (DFT) code SIESTA²³, the optimum geometries of isolated **11**, **12** and **13** were obtained by relaxing the molecules until all forces on the atoms were less than 0.05 eV / Å (Figure S38). We used a double-zeta plus polarization orbital basis set, norm-conserving pseudopotentials, the local density approximation (LDA) exchange correlation functional, and in order to define the real-space grid, an energy cut-off of 250 Rydbergs. We also computed the results using GGA and found that the resulting transmission functions were comparable with those obtained using LDA.²⁴⁻²⁵ To simulate the likely contact configuration during a break-junction experiment,²⁶⁻²⁷ we employed leads constructed from 6 layers of Au (111), each containing 30 gold atoms, and further terminated with a pyramid of gold atoms in two junctions and flat leads in another junction (Figure 4). After relaxing each molecular junction in four different junction geometries, we calculated the electrical conductance using the Gollum quantum transport code.²⁸

We performed DFT quantum transport calculations, exploring both the thiomethyl (Au-SMe) contact geometry and the Au-H direct contact. Figure S39 shows that **12** does not bind to gold through H atoms, which explains why **12** does not form a junction in the STM-BJ measurements. On the other hand, binding energy calculations for **11** and **13** suggest that they bind preferentially through their thiomethyl groups, and π -gold interactions are not favored. (Figures S40 and S41). This reduction in the π -stacked binding energy can be attributed to the torsional angles of the phenyl groups resulting in non-planar molecules, as shown in Figure 1.

As described in the SI (see Figure 4), four different junction geometries corresponding to different connectivities to gold electrodes were explored for each of **11** and **13**. The resulting transmission coefficients for these four geometries of **11** and **13** are shown in Figure S45.

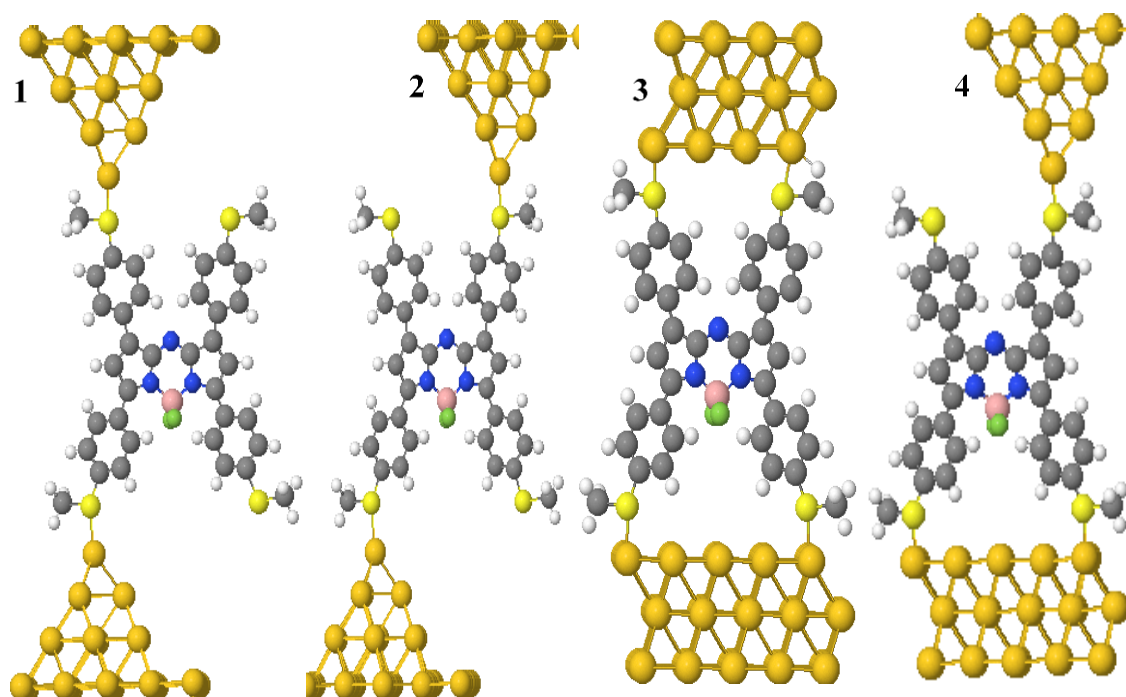


Figure 4. **11** in junctions, four possible geometries: 1, 2, 3 and 4 (respectively).

It is well known that DFT frequently underestimates the HOMO-LUMO gap²⁹⁻³⁰ and from Table S16 in the Supporting Information it is clear that the calculated gaps are less than the optically-measured gaps. To overcome this deficiency, a scissor correction³¹ is performed by diagonalizing the molecular sub-matrix of the full Hamiltonian, then shifting the eigenvalues above the Fermi energy such that the new HOMO-LUMO gap matches the experimental value of the isolated molecule, (see Table S16). Finally, the diagonalized matrix is transformed back

to the original basis to obtain the corrected full Hamiltonian (for more details see³²⁻³³).

Transmission coefficients after scissor corrections are shown in Fig. 5.

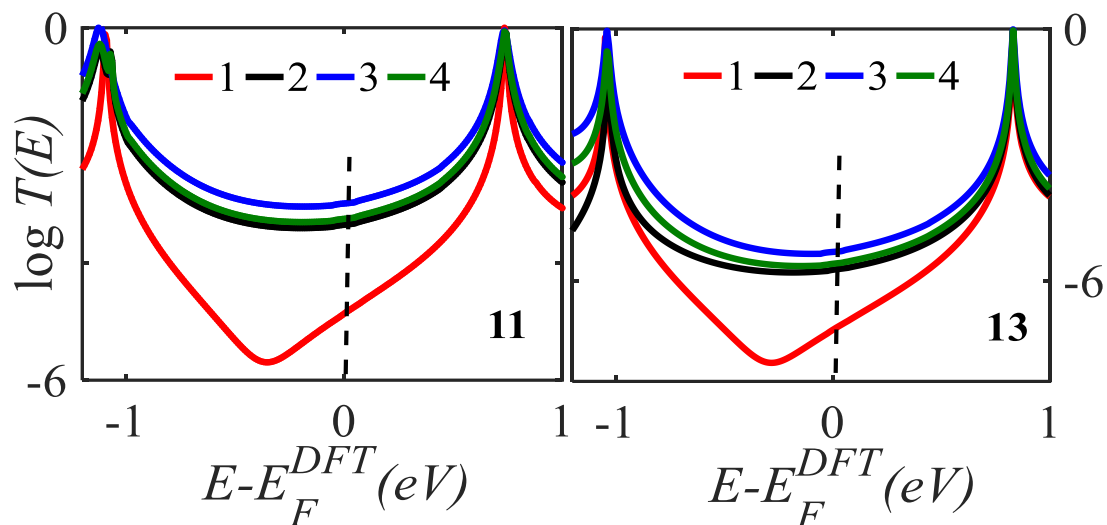


Figure 5. Transmission coefficients $T(E)$ of **11** (left) and **13** (right) for four different possible geometries using scissors corrections (see Figure 4).

Figure 5 shows that connectivities 2, 3 and 4 produce constructive quantum interference (CQI) for both **11** and **13** (Figure 4), while geometry 1 yields destructive quantum interference (DQI), signified by the presence of a dip in the red curves near the middle of the HOMO-LUMO gaps (i.e. near $E = -0.3\text{eV}$). To obtain electrical conductances from these transmission curves, a value for the Fermi energy is needed. Literature comparisons between theory and experiment reveal that in the presence of nitrogen heteroatoms, DFT invariably predicts that the Fermi energy lies close to the LUMO resonance (as shown in Figure S45), whereas agreement with experiment is obtained only when the Fermi energy is chosen to be close to the middle of the HOMO-LUMO gap.³⁴⁻³⁸ In agreement with these studies, we also find that the closest agreement between our theory and experiment is obtained for a Fermi energy located near the mid-gap, as indicated by the dashed lines in Figure 5. The corresponding room-temperature conductances

are shown in Table 4. For comparison with experiment, Table 4 also shows the average value of these four conductances of **11** and **13** ($E_F^{DFT} \approx$ mid gap).

To demonstrate that DQI is present in the π system of the aza-BODIPY core for connectivity 1, whereas CQI is present for connectivities 2-4, a simple tight binding model is presented in the SI, which reproduces the qualitative features of DFT transmission curves (For more detail see section 10 of the SI).

Table 4. Experimental and theoretical conductance values of compounds **11-13** for the four geometries 1, 2, 3 and 4 shown in Figure 4. The theoretical values shown in parentheses are obtained without a scissor correction. Theoretical values obtained after a scissor correction are not enclosed by parentheses.

M	Conductance (G/G ₀)		Conductance (G/G ₀) for the four geometries				
	Experiment		Theory ($E_F^{DFT} \approx$ mid gap)				
	THF/Mesitylene	CHCl ₃ /Air	1	2	3	4	Average
11	4.0×10 ⁻⁴	2.1×10 ⁻⁴	(9.5×10 ⁻⁶)	(1.6×10 ⁻⁴)	(4.1×10 ⁻⁴)	(2.2×10 ⁻⁴)	(2.0×10 ⁻⁴)
			1.0×10 ⁻⁵	3.4×10 ⁻⁴	7.8×10 ⁻⁴	4.3×10 ⁻⁴	3.8×10 ⁻⁴
13	2.5×10 ⁻⁵	2.7×10 ⁻⁵	(1.6×10 ⁻⁶)	(4.8×10 ⁻⁵)	(1.2×10 ⁻⁴)	(7.5×10 ⁻⁵)	(6.3×10 ⁻⁵)
			1.0×10 ⁻⁶	1.6×10 ⁻⁵	3.7×10 ⁻⁵	2.1×10 ⁻⁵	2.0×10 ⁻⁵

CONCLUSION

We have measured and computed the electrical conductance of three closely related tetraphenyl-aza-BODIPY-based molecules. Molecules **11** and **13** with four thiomethyl anchors form stable contacts within our BJ-STM, with conductance values of $4.1 \cdot 10^{-4} G_0$ and $2.5 \cdot 10^{-5} G_0$, respectively. The lower conductance of the latter correlates with the increased length of **13** compared with **11**. On the other hand, **12**, having only two distal thiomethyl anchor groups, displayed no detectible conductance. Density functional theory-based calculations reveal that

transport takes place through phase-coherent tunneling near the middle of the HOMO-LUMO gap. For each molecule, four connectivities to the thiomethyl anchors were considered, with three of the four exhibiting constructive quantum interference, with rather flat transmission functions near the gap center, and one exhibiting destructive interference, signified by a transmission dip near the gap center. Although the measured electrical conductance reflects an average of all four possible connectivities, as shown in table 4, the low-conductance configurations corresponding to destructive quantum interference do not make a significant contribution to the average. Therefore, our study reveals that while transport through these molecules results from a combination of both constructive (involving the aza-BODIPY core) and destructive quantum interference (through the proximal and distal thioanisoles attached to the same pyrrole), the average conductance is dominated by configurations exhibiting constructive quantum interference. To highlight the role of quantum interference in the tetraphenyl-aza-BODIPY core, a simple tight binding model (TBM) was employed.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, NMR spectra, crystallographic, conductance details and computational details. Raw Break-Junction spectroscopy are available at the Data Catalogue:

<https://doi.org/10.17638/datacat.liverpool.ac.uk/973>

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Notes

The authors declare no competing financial interest.

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