

# **CHEMISTRY** A European Journal



# **Accepted Article** Title: Regioisomeric BODIPY-Benzodithiophene Dyads and Triads with NIR Tunable Emission as Ratiometric Thermometers and Molecular Viscometers Authors: Aswathy Plakkal Rajeev, Sushil Sharma, Narendra Pratap Tripathi, and Sanchita Sengupta This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article. To be cited as: Chem. Eur. J. 10.1002/chem.201902952 Link to VoR: http://dx.doi.org/10.1002/chem.201902952 **Supported by** ACES

ACES

WILEY-VCH

# Regioisomeric BODIPY-Benzodithiophene Dyads and Triads with Tunable Red Emission as Ratiometric Temperature and Viscosity Sensors<sup>†</sup>

Aswathy P. R.<sup>‡</sup>, Sushil Sharma<sup>‡</sup>, Narendra Pratap Tripathi and Sanchita Sengupta<sup>\*[a]</sup>

Abstract: Regioisomeric acceptor-donor (AD) molecular rotors (**p**-AD, **m**-AD and **m**-ADA) were synthesized and characterized where dyads **p**-AD and **m**-ADA and triad **m**-ADA contained BODIPY and Benzodithiophene (BDT) as electron acceptor and donor respectively. In all the compounds, the donor and acceptor moieties are electronically decoupled by a phenyl spacer, either through a para coupling or through a meta coupling. The dyad counterparts **p**-AD and **m**-AD showed distinct photophysical characteristics where dyad **p**-AD showed TICT band at ~ 654 nm characterized by a Stokes shift of ~ 150 nm and prominent solvatochromism. However, meta regioisomeric triad **m**-ADA showed well-defined aggregation in solution. Notably, owing to temperature tunable and solvent viscosity dependent emission, efficient ratiometric temperature sensing with positive and negative temperature coefficients and viscosity sensing was observed for all compounds. Interestingly, fluorescence of dyad **m**-AD (in 10/90 v/v THF/water) revealed a near white light emission with CIE chromaticity coordinates (x, y) of (0.32, 0.29). Furthermore, fluorescence emission of **p**-AD in THF at 0 °C also showed a near white light emission with chromaticity coordinates (x, y) of (0.34, 0.27). Such multifunctional rotors with readily tunable emission in red region and prominent temperature and viscosity sensing abilities are promising for sensing and bioimaging applications.

### Introduction

Design of ratiometric fluorescent molecular probes for temperature detection is an emerging research area having witnessed tremendous progress in the last decade.<sup>[1,2]</sup> Ratiometric temperature and viscosity molecular probes play a vital role in accurate (bio)molecular detection, sensing, imaging and theranostic applications.<sup>[3]</sup> Such ratiometric molecular probes have low sensitivity to external factors and thus, high spatio-temporal resolution and accuracy.<sup>[1,2]</sup> Moreover. fluorescent molecular temperature/viscosity sensors are advantageous for biological applications due to their noninvasive nature.<sup>[3]</sup> Among the various design strategies for small organic molecule based ratiometric temperature and viscosity probes,<sup>[4]</sup> donor-acceptor (D-A) rotor molecules<sup>[5]</sup> that show twisted intramolecular charge transfer (TICT) are of particular interest.<sup>[4,6-9]</sup> In recent years, multifunctional donor-acceptor pronounced TICT rotors with large Stokes shift, solvatochromism, aggregate induced emission, temperature and viscosity sensing have been reported.[9-11] The rational design of a multichromophoric rotor is a complex task because the emission of TICT rotors are governed by the subtle equilibrium between planar and twisted conformations in excited states, often non-trivial to predict computationally.<sup>[12]</sup> Owing to the large Stokes shift of TICT rotors, minimal overlap occurs between their absorption and emission leading to least reabsorption.<sup>[1,2]</sup> As a result, an improved signal-to-noise ratio can be achieved while utilizing such TICT rotors for fluorescence imaging.<sup>[1,2]</sup> Owing to the inherent dual emission due to TICT and local excited (LE) states, and sensitivity of their emission to solvent polarity and temperature, such molecules show pronounced ratiometric temperature sensing behavior.<sup>[1,2]</sup> Moreover, as a consequence of multiple emission, such rotors exhibit other

 <sup>[a]</sup>Aswathy P. R., S. Sharma, N. P. Tripathi and Dr. S. Sengupta Department of Chemical Sciences, Indian Institute of Science, Education and Research (IISER) Mohali, Punjab 140306, India.
 <sup>[a]</sup>Email: <u>sanchita@iisermohali.ac.in</u>
 <sup>†</sup>Supporting Information for this article is given via a link at the end of the document.

<sup>‡</sup> Contributed equally.

properties such as white light emission<sup>[13,14]</sup> desirable for (opto)electronic applications. The emission of these rotor molecules can be further tuned through aggregate induced emission (AIE)<sup>[15,16]</sup> and mechanochromism.<sup>[17]</sup> TICT rotors are promising viscosity probes because they exhibit emission enhancement due to restricted intramolecular rotation in solvents of increasing viscosity.<sup>[10,11,18–20]</sup> Examples of ratiometric temperature and/or viscosity<sup>[8,11]</sup> sensors based on TICT rotors involve fluorophores such as tetraphenylethylenes (TPE),<sup>[4]</sup> indocyanines,<sup>[10,21]</sup> porphyrins,<sup>[22]</sup> 4,4-difluoro-4-bora-3a,4a-(BODIPY),<sup>[23–27]</sup> arylboranes.[28] N,Ndiaza-s-indacene dimethylaniline based compound<sup>[29]</sup> and many others.<sup>[25,26,30-35]</sup> Luminescent thermometers based on molecular rotors are being intensively investigated for temperature sensing of cellular microenvironments as well as of microfluidic devices.[36] In recent years, TICT rotors<sup>[25]</sup> based on the BODIPY dyes<sup>[37-40]</sup> have been utilized efficiently for temperature sensing<sup>[9]</sup> as well as for imaging of cellular local micro viscosity using fluorescence lifetime imaging (FLIM). However, red emissive BODIPYs<sup>[41-43]</sup> and with temperature and viscosity sensing capability are extremely rare in literature.[44]

Challenges in the development of ratiometric temperature/viscosity molecular probes for sensing and especially for bioimaging applications include development of photostable rotors with red emission for deeper tissue penetration and large Stokes shift for least autofluorescence.<sup>[3,45,46]</sup> Significant efforts have been ongoing in the development of TICT with large Stokes shift, red emission and possessing ratiometric temperature/viscosity sensing capabilities.<sup>[22,33,47-51]</sup> Kuimova et al. reported porphyrin dimers (red em. ~ 780 nm, Stokes shift ~ 300 nm), uniquely constructed for sensing of viscosity by ratiometric or lifetime-based methods, in solvents of different viscosity at different temperatures.<sup>[22]</sup> Mallard et al. reported glycoconjugated porphyrin dimers (red em. ~ 740-800 nm) for ratiometric temperature sensing.<sup>[48]</sup> Other notable examples of rotors for ratiometric sensing with emission around ~ 630-650 nm are the T-shaped pyridoquinoxaline (PQCz-T) rotor (red em. 635 nm, Stokes shift ~ 195 nm),[49] dimalononitrile-dicarbazole-substituted 1,4-butadiene (MCBD)[51] (red em. 640 nm, Stokes shift ~ 80 nm) and pentamethine cyanine Ry3 (red em. 650 nm, Stokes shift 250 nm).<sup>[33]</sup> Very recently, Tang and co-workers adopted an approach to design AD'DD'A type rotor based on benzo-bisthiadiazole and triphenylamine (TPA) and thiophene spacer that showed unique

TICT behavior in aggregated state with emission in near infra red (NIR) window II (900-1500 nm).<sup>[50]</sup> In many of these examples, temperature sensitivity in wide working temperature range were obtained, as comprehensively reviewed in a recent literature.<sup>[49]</sup> Notably, rotors with positive temperature coefficients in this context are extremely desirable because the increase in emission intensities with temperature can significantly supress background interference at high temperatures and thus are advantageous for sensing/imaging purpose.<sup>[29]</sup> Interestingly however, rotors showing positive temperature coefficients are rather few.<sup>[28,29,49,51,52]</sup>

Recently, we reported an acceptor-donor-acceptor (**p-ADA**, Figure 1) type triad rotor consisting of BODIPY acceptor and benzodithiophene (BDT) donor that showed efficient TICT with Stokes shift of ~ 194 nm (red em. upto 700 nm), the highest known Stokes shift for BODIPY compound and charge carrier mobility of ~  $4.45 \times 10^{-4}$  cm<sup>-2</sup>/Vs.<sup>[53]</sup> The D and A units were connected at the para positions of the two phenyl spacers thus, it was named **p-ADA** (Figure 1).<sup>[53]</sup> Interestingly however, studies on the effect of regioisomerism in relation to TICT/AIE in organic rotor molecules are rather few.<sup>[49,54–58]</sup> To the best of our knowledge, regioisomeric BODIPY based multichromophoric TICT rotors with large Stokes shift, tunable emission in red region and unique temperature and viscosity sensing capabilities have not been reported.

To bridge this knowledge gap, we present synthesis of new regioisomeric triad m-ADA and new dyads p-AD and m-AD (Figure 1). We intend to study the effect of regioisomerism (para- vs. meta- connectivity of phenyl spacer to D and A) on TICT, AIE and temperature as well as viscosity sensing properties of these compounds. Their optical properties such as UV/Vis absorption, fluorescence, fluorescence solvatochromism, aggregate induced emission, viscosity and temperature dependent emission have been investigated in-depth. By utilizing the TICT and LE emissions, we present ratiometric temperature sensors based on these BODIPY-BDT regioisomers that possess either positive or negative temperature coefficients depending upon the solvent of study. Furthermore, chromaticity analysis for some of these molecules revealed near white light emission that justify their multifunctionality for possible applications in (opto)electronics.



Figure 1. Chemical structures of regioisomeric ADA triads m-ADA, p-ADA and dyads p-AD and m-AD synthesized and investigated in this work.

### **Results and Discussion**

#### Synthesis

The synthesis of dyads **p-AD** and **m-AD** and triad **m-ADA** were performed as outlined in Scheme 1. In order to achieve the

10.1002/chem.201902952

### WILEY-VCH

regioisomeric meta- and para-dyads and meta-triad, the corresponding meta- and para-bromo BODIPYs were synthesized. Regioisomers BDP-p-Br and BDP-m-Br were starting from 4-bromobenzaldehyde and 3synthesized bromobenzaldehyde respectively and pyrrole in the presence of catalytic amount of HCl in an aqueous medium to yield corresponding dipyrromethane (DPM) compounds according to a reported procedure for a different DPM.<sup>[53,59,60]</sup> Subsequently, corresponding BODIPY BDP-p-Br and BDP-m-Br were synthesized in 69 % and 19% respectively (see supporting information for synthetic procedures and characterization).<sup>[53]</sup> Distannylated BDT (D2) was synthesized according to a previously reported procedure starting from thiophene-3carboxylic acid.<sup>[61]</sup> Furthermore, with the intention to synthesize dyad compounds for which monostannylated BDT was required, some optimization reactions were performed and mixture of monostannylated and distannylated BDT (D1+D2) was obtained (see supporting information). The isolation of monostyannylated BDT was challenging owing to its negligible difference in R<sub>f</sub> values from the distannylated or the starting compound. The synthesis of m-ADA was achieved by Stille coupling of BDP-m-Br and D2 in dry toluene with catalytic tris(dibenzvlidene-acetone) dipalladium(0) amounts of (Pd2(dba)3) and tri(o-tolyl)phosphine (P(o-tol)3) under an inert atmosphere and m-ADA was isolated in 54 % yield (supporting infromation for details). Syntheses of dyads m-AD and p-AD were achieved under similar Stille coupling conditions using D1+D2 as donor and BDP-m-Br and BDP-p-Br as acceptors respectively in low yields of 14 % and 11 %.



Scheme 1. Synthesis of dyads  $m\mbox{-}AD$  and  $p\mbox{-}AD$  and triad  $m\mbox{-}ADA.$ 

The synthesized compounds were purified by column chromatography as well as preparative thin layer chromatography (TLC) using petroleum ether/ethyl acetate or dichloromethane (DCM) mixtures (v/v) as eluents. All precursors and **m-ADA**, **p-AD** and **m-AD** were characterized with <sup>1</sup>H NMR, <sup>13</sup>C NMR and high resolution mass spectrometry (HRMS) (details provided in supporting information).

#### Absorption and Emission

UV/Vis and fluorescence spectra were recorded for all compounds in chloroform (CHCl<sub>3</sub>) at a concentration of  $10^{-5}$  M. Figure 2a shows the comparative UV/Vis absorption spectra of triad **m-ADA** and dyads **m-AD** and **p-AD** in CHCl<sub>3</sub> ( $c \sim 10^{-5}$  M) and the absorption profiles of model acceptors BDP-m-Br and BDP-p-Br and donor alkylated BDT, are provided in Figure S1, supporting information. The absorption spectra of m-ADA, m-AD and p-AD were compared with their corresponding monomer units, i.e., donor and acceptor units. All compounds have three major peaks corresponding to BODIPY (~ 504 nm), BDT (~ 312-322 nm), and broad peak around ~ 360-380 nm corresponding to extended conjugation of phenyl unit with BDT (Figure 2a). Peaks around ~ 504 nm correspond to BODIPY S<sub>0</sub>-S<sub>1</sub> transition and peaks around 312-322 nm correspond to BDT  $\pi$ - $\pi$ \* transition. Notably, no electronic communication was observed between BDT and BODIPY since their corresponding peak positions were maintained in the dyads p-AD and m-AD and triad m-ADA. This observation is in agreement with density functional theory (DFT) calculations (vide infra) revealing compartmentalization of HOMO and LUMO on the donor and acceptor respectively. Owing to the weaker coupling of m-phenyl with the BDT unit in m-ADA and m-AD compared to the coupling in p-phenyl with BDT (in p-AD), peak splitting to a greater extent was observed in meta compounds (Figure 2a) than in para compound p-AD. Similar peak splitting occurring in meta-regioisomer and its absence in para-regioisomer has been reported earlier.<sup>[53]</sup> The fluorescence emission spectra of p-AD in CHCl<sub>3</sub> were measured upon excitation at two wavelengths 377 nm (donor) and 504 nm (acceptor) in Figure 2b. Excitation at 377 nm led to emission at 410 nm and 430 nm from donor, 516 nm from acceptor and a broad but intense band around ~ 654 nm corresponding to a TICT state and a Stokes shift of ~ 150 nm (Figure 2b).



Figure 2. a) Comparison of absorption spectra for m-AD, p-AD, m-ADA in CHCl<sub>3</sub> (c ~  $10^{-5}$  M), b) Normalized emission spectra for m-AD, p-AD, m-ADA in CHCl<sub>3</sub> (c ~  $10^{-5}$  M) upon exciting at 362 nm, 377 nm, and 380 nm respectively.

In comparison to **p-ADA** that showed Stokes shift of 194 nm,<sup>[53]</sup> the Stokes shift of **p-AD** was ~ 150 nm which was 44 nm less than that of **p-ADA**. Fluorescence emission spectra of **m-ADA** were measured upon three different wavelengths, 322 nm, 380 nm (donor) and 504 nm (acceptor) respectively. Upon excitation at 322 nm and 380 nm, donor emission at 430 nm, acceptor emission at 517 nm and a broad but less intense band around ~ 662 nm were observed. The band around ~ 662 nm can be attributed to aggregation and this band was observed in the emission spectra of other solvents also (vide infra). In case of **m-AD**, three distinct emission peaks were observed. Upon excitation at 362 nm (donor) and 504 nm (acceptor), a donor emission peak at 430 nm and acceptor emission at 522 nm were observed. A broad but a weaker TICT type band was observed around ~ 645 nm that was also observed in tetrahydrofuran

(THF). Subsequent to steady state emission measurements, fluorescence quantum yields were determined for **p-AD**, **m-AD** and **m-ADA** in CHCl<sub>3</sub> by relative method using Rhodamine B as the reference compound in ethanol (Table S1) and low quantum yields of ~ 0.031, 0.021 and 0.035 were obtained for **p-AD**, **m-AD** and **m-ADA** respectively. TICT compounds are usually known to have low fluorescence quantum yields owing to the forbidden nature of the transition from the v = 0 vibrational level of the TICT state to the ground state.<sup>[4]</sup>

#### **Quantum Chemical DFT Calculations**

In order to gain insights about the frontier molecular orbitals (FMOs) as well as torsion angles of m-ADA, m-AD and p-AD, DFT calculations were performed using the Gaussian 09 package (see reference S1, supporting information) by the B3LYP/6-31G(d,p) method. The torsional angles in m-ADA between the BODIPY and phenyl spacer ( $\Phi_1$ ,  $\Phi_4$ ) and between phenyl spacer and BDT ( $\Phi_2,\,\Phi_3)$  were ~ 55.4°, 54.2° and ~ 22.5° 22.5° respectively (Table S2, S3) confirming the non-planarity of this molecule. The calculated HOMO and LUMO energy levels of m-ADA were -5.39 eV and -2.87 eV respectively, with the LUMO and LUMO+1 being energetically degenerate (Figure 3). FMO composition analysis for triad m-ADA indicated major contribution of BDT in the HOMO (91 % contribution, table S4, figure S3) and BODIPY contributing towards the LUMO level (91 %, table S4) with no overlap between the HOMO and LUMO (Figure 3). Therefore, no electronic communication was present between BDT and BODIPY as confirmed by experimental absorption spectrum of m-ADA. Similar localization of HOMO and LUMO of m-AD and p-AD on BDT and BODIPY respectively led to electronic decoupling of BDT and BODIPY units (Figure 3, Table S4). However, coupling of phenyl ring with BDT was present in all cases and this coupling is different in m-ADA/m-AD and p-ADA/p-AD that is reflected in their optical properties. The DFT calculated HOMO and LUMO levels of p-AD were at -5.33 eV and -2.83 eV respectively. Torsion angles between the BODIPY and phenyl ( $\Phi_1$ ) and between phenyl and BDT ( $\Phi_2$ ) in m-AD were 55.2° and 23.3° respectively while in p-AD they were 52.3° and 22.9° respectively (Figure 3, Table S2).



Figure 3. DFT calculated (B3LYP/6-31G(d,p)) geometry optimized structures of **p-AD**, **m-AD** and **m-ADA** with indication of torsion angles and HOMO/LUMO levels.

In order to obtain insights about the redox properties and FMO energies for dyads and triad, cyclic voltammetry (CV) measurements were performed for **p-AD**, **m-AD** and **m-ADA** as well as for the model subunits **BDP-p-Br**, **BDP-m-Br** and alkyl BDT in dry DCM (Figure S3, Table S5 and S6). From CV studies, the HOMO levels were calculated to be -5.88 eV, -5.91 eV and -5.61 eV for **p-AD**, **m-AD** and **m-ADA** respectively. Corresponding LUMO values of -4.12 eV, -4.20 eV and -4.22 eV

were obtained for **p-AD**, **m-AD** and **m-ADA** respectively. Thus, CV studies substantiate the theoretically calculated FMO energy levels as well as the fact that BDT and BODIPY serve as electron donor and acceptor respectively in all dyads and triad.

#### Fluorescence Solvatochromism

Since compound p-AD showed the formation of a TICT state, fluorescence solvatochromism was investigated in order to assess the polarity of the ground and first excited state.<sup>[4,6]</sup> Emission maximum of p-AD in toluene was observed at ~ 530 nm which was due to local excited (LE) emission since toluene being a non-polar solvent can not stabilize the TICT state with high dipole moment. A bathochromically shifted band at ~ 654 nm was observed in CHCl<sub>3</sub> arising due to TICT state (Figure 4a). The ground state of p-AD has a smaller dipole moment than the excited state, because UV-VIS absorption spectra of molecule in solvents of different polarities did not show any change in the absorption maxima (Figure S4). Notably, the TICT band was non-existent in high polarity solvents acetonitrile (ACN) and methanol (MeOH) owing to the limited solubility of the compound in these solvents and in DCM due to rapid non-radiative deactivation. These observations are consistent with similar TICT rotors that show negligible emission in ACN and MeOH.<sup>[49]</sup> Formation of TICT state in p-AD was justified from DFT calculated torsion angles that indicate the non-planarity of the compound. This results in twisting around the BODIPY-phenyl single bond in the excited state leading to pronounced charge separation of D and A units accompanied by an increase in the dipole moment in the excited state. The fluorescence solvatochromism was further probed in binary solvent mixtures of hexane/THF (v/v) by sequentially increasing the percentage of THF from 10% to pure THF and thus achieving a wide range of solvent polarity. Interestingly, when the solvent polarity was decreased from 100 % THF sequentially 99/1 (v/v) hexane/THF, the band at 647 nm shifted to ~ 523 nm (through a broad band at ~ 580 nm corresponding to an intermittent LE state) (Figure 4b, e). Thus, a pronounced hypsochromic shift upon decreasing solvent polarity substantiates the formation of TICT state in p-AD. Interestingly, the meta counterpart m-ADA of previously published p-ADA compound<sup>[53]</sup> does not show any TICT in various solvents. Solvent polarity dependent absorption measurements did not show significant variations as shown in Fig The absence of any TICT in m-ADA could be attributed to a weaker electronic coupling between the D and A units through the meta positions of the phenyl.<sup>[54,58]</sup> Solvent polarity dependent fluorescence spectra of m-ADA showed apart from the BODIPY emission at 530 nm, a weaker peak at ~ 662 nm in THF, toluene and DCM and a peak at ~ 675 nm in MeOH (Figure 4c). The peak position of this band remained unchanged in polar and non-polar solvents indicating that this peak did not result from TICT but presumably due to the aggregate formation at low concentrations (c ~  $10^{-5}$  M). The m-phenylene connection in m-**ADA** restricts the free rotation of phenyl ring and so the  $\pi$ - $\pi$ stacking is probably favored for this compound. Furthermore, in **m-ADA** the comparable terminal twist angles ( $\Phi_1$  and  $\Phi_4$ ) of 55.4° and 54.2° to **p-ADA** and smaller  $\Phi_2$  and  $\Phi_3$  of 22.5°, 22.5° than p-ADA (32.2°, 32.2°) renders the molecule more planar than p-ADA. Thus, m-ADA being less twisted than p-ADA has presumably a higher propensity to form intermolecular  $\pi$ -stacks. Similar solvatochromism studies were performed for m-AD and a weaker but a broad band around ~ 643 nm was observed only in CHCl<sub>3</sub> and THF which could be attributed to a very weakly emissive TICT-type transition (Figure 4d).

Fluorescence lifetime measurements were performed for p-AD, m-AD and m-ADA in CHCl<sub>3</sub> using time correlated single

10.1002/chem.201902952

WILEY-VCH

photon counting (TCSPC) measurement technique (Figure S5). The fluorescence lifetime of p-AD, m-AD and m-ADA were measured upon an excitation with 375 nm laser diode. Decay profiles at emission wavelengths of 430 nm (corresponding to donor decay) and TICT emission at 647 nm were studied for p-AD. The decay corresponding to charge transfer emission is known to exhibit a longer rise time characteristic of charge transfer and a slower component characteristic of the lifetime of the equilibrated molecules.<sup>[7,58]</sup> Moreover, in the decay profile of the CT band, a growth component can be observed (Fig. S5c) which is well known for fluorescence decay of TICT molecules.<sup>[58]</sup> Accordingly, a slower decay was observed for **p**-AD emission at 647 nm with a lifetime of ~ 3 ns than the decay at 430 nm (lifetime of ~ 0.42 ns) as shown in Figure S5c. The average lifetimes of the decay corresponding to 430 nm and 647 nm were ~ 0.7 ns and ~ 1.83 ns respectively. The decay at 430 nm is in close agreement with the neat donor decay with lifetime of ~ 0.8 ns reported earlier.[53]



Figure 4. Normalized fluorescence emission spectra of p-AD a) upon excitation at 377 nm in solvents of different polarity; b) in different hexane/THF (v/v) solvent mixtures; c) Fluorescence emission spectra of m-ADA and d) m-AD upon excitation at 380 nm and 362 nm respectively in different solvents; e) Fluorescence solvatochromism of p-AD in hexane/THF mixtures (from left to right: 99/1, 90/10, 80/20, 70/30, 60/40, 50/50 v/v hexane/THF) under handheld UV lamp of wavelength 365 nm.

Similarly, the fluorescence lifetimes of **m-ADA** at emission wavelengths of 432 nm (donor emission) and 662 nm (aggregate emission) were ~ 0.88 ns and ~ 5 ns respectively. Such distinct decay profiles for **m-ADA** and **m-AD** indicate the presence of two or more distinct species/conformer in the solution and the fact that all the decays could be fitted with biexponential or tri-exponential functions substantiates the presence of multiple conformers or species in the solution. The fluorescence decays as well as fitted plots with fitting parameters and lifetimes are presented in Figure S5 and Table S7.

#### **Aggregation Induced Emission (AIE)**

Aggregate induced emission (AIE) property was investigated in dyads p-AD and m-AD and triad m-ADA by measuring

fluorescence in binary mixture of water and THF. In case of p-AD, starting from pure THF when the water fraction was increased to 10 vol% up to 50 vol%, the fluorescence intensity decreased drastically (Figure 5a). This can be attributed to the increasing polarity of the solvent mixture upon increasing the water content that favours TICT and therefore non-radiative deactivation. However, upon further increasing the water fraction from 60 vol% onwards i.e., 60/40, 70/30, 80/20 and 90/10 v/v water/THF, fluorescence intensity increased up to two to three times than the intensity at 10/90 v/v water/THF. The increased fluorescence intensity can be attributed to the formation of wellwithout any defined nanoaggregates, agglomeration or precipitation, which restrict the intramolecular rotation. For m-ADA the fluorescence intensity increased for 90/10 and 80/20 (v/v) in THF/water than from pure THF. Further it uniformly decreased upon increasing percentage of water. A new band around ~ 670 nm was observed due to aggregation upon increasing the water percentage (Figure 5b). In case of m-AD, it followed the similar behaviour as in p-AD. It decreased first and upon increasing the water content from 30% onwards, the intensity started increasing (Figure 5c) (corresponding UV/Vis of p-AD and m-AD in Figure S6).

The solutions of **m-ADA** in THF/water (v/v) showed sharp colour change from orange to pink as the solvent is changed from 100% THF to 90/10 (v/v) water/THF (Figure 5d, inset) due to aggregate formation. Upon changing the solution composition from 60/40 (v/v) THF/water to 50/50, the aggregation is evident from appearance of a bathochromically shifted new band at 550 nm in absorption spectra (Figure 5d) and a colour change from orange (monomer) to pink (aggregates). Interestingly triad **m-ADA** has no propensity for TICT owing to much weaker electronic coupling of meta phenylene spacer and probably a higher barrier for TICT and planar states.



Figure 5. Aggregate induced emission in a) p-AD, b) m-ADA, and c) m-AD in different mixture of water/THF. d) Absorption of m-ADA in water/THF mixture. e) CIE Chromaticity plot of m-AD in water/THF showing a single component near-white light emission (0.32, 0.29) at 10/90 (v/v) THF/water mixture. Inset in (d): Solutions of m-ADA in THF/water (v/v) left to right: 90/10, 80/20, 70/30, 60/40, 50/50, 30/70, 20/80, 10/90 showing AIE effect.

10.1002/chem.201902952

WILEY-VCH

Interestingly, chromaticity analysis for the emission of **m-AD** in all the water/THF solvent mixtures showed emission colours distributed in the blue, green and purple region (Figure 5e). A chromaticity analysis using Internationale de l'Eclairage (CIE) coordinates revealed a near-white light emission component with chromaticity coordinates of x = 0.32, y = 0.29 (Figure 5e) for 10/90 (v/v) THF/water solution. Pure white light emissive singular compounds (with x, y coordinates of 0.33, 0.33) are rare<sup>[13,14,62-64]</sup> and easily tunable emission in blue, green and purple region are rare to obtain in a single compound. This is achievable in the present case through molecular design and only by changing solvent compositions.

### Temperature Induced Tunable Fluorescence

The emission of molecular rotors are highly sensitive to solvent temperature and show different emission properties upon varying the temperature. Temperature sensing in rotor molecules originates from two decay channels corresponding to the twisted and planar molecular conformations in the excited state.<sup>1</sup> In order to obtain insights about the temperature sensitivity of fluorescence of these dyads and triads, temperature-dependent fluorescence were performed for **p-AD**, **p-ADA**, **m-AD** and **m-ADA** in various solvents. Emission measurements were performed in the temperature range of -20 °C upto 85 °C (depending upon the boiling point of the chosen solvent) in quartz cuvettes in a cuvette holder thermally equilibrated using a Peltier thermostat.

In **p-AD**, upon increasing the temperature from -20 °C to 55 °C in CHCl<sub>3</sub>, a drastic increase in the fluorescence intensity was observed and the TICT band was blue shifted from ~ 670 nm to ~ 636 nm (Figure 6a). This observation is attributed to the fact that heating helps in crossing the activation barrier from TICT to the LE state and the LE state gets more populated thereby causing the hypsochromic shift in the emission band and increased intensity. For **p-AD**, temperature dependent fluorescence measurements in THF (Figure 6b) also showed increase in the TICT band intensity and a concomitant blue shift. The effect of temperature on **p-AD** in toluene however was different as evident from Figure 6c.



Figure 6. Temperature dependent fluorescence emission spectra of dyad p-AD in a) CHCl<sub>3</sub>; b) THF and c) Toluene; d) CIE chromaticity plot of temperature dependent emission of p-AD in THF showing a near-white light emission at 0°C (CIE coordinates of 0.33, 0.27), 5 °C (0.34, 0.27) and 10 °C (0.35, 0.27).

In toluene, the TICT band was absent and the spectra showed two bands at 530 nm corresponding to the BODIPY emission and ~ 580 nm corresponding to an intermittent LE state at low temperatures. Upon increasing the temperature, the emission intensity decreased due to enhanced molecular motions and possibility of non-radiative decay channels. Interestingly, there was no change in absorption spectra with the variation of temperature ruling out any possibility of degradation of the compounds (Figure S7). Temperature dependent fluorescence of p-AD in 2-methyl THF (2MeTHF) was also performed in the temperature range of -15 °C to 75 °C as shown in Figures S8, S9. Figure 6d shows the CIE chromaticity plot for temperature dependent emission of p-AD in THF. Interestingly, at temperatures of 0 °C, 5 °C and 10 °C, near white light emission with CIE coordinates (x, y) of (0.33, 0.27), (0.34, 0.27) and (0.35, 0.27) respectively were obtained (Figure 6d). Temperature dependent emission spectra were measured for p-ADA in DCM, THF, toluene and 2MeTHF in the temperature range from -15 °C upto the boiling point of the respective solvents (Figure 7a-d). The TICT band of p-ADA initially observed at ~ 700 nm in DCM was blue shifted upto 678 nm accompanied by an increase in the emission intensity upon increasing temperature upto 35 °C. In THF, the TICT band initially located at ~ 660-670 nm was blue-shifted upto ~ 645 nm upon increasing the temperature to 50 °C. Temperature dependent emission measurements for p-AD and p-ADA were performed in 2MeTHF because this solvent forms a glassy matrix at cryogenic temperature (-196 °C) and thus, can reveal the complete confinement of LE state at -196 °C.<sup>[65]</sup> Temperature dependent emission for compounds p-ADA and p-AD in 2MeTHF showed two different trends in the lower temperature range (25 °C to -15 °C) (Figure S10) and in higher temperature range (25 °C to 75 °C) (Figure 7d, Figure S11). When temperature was reduced from 25 °C to -15 °C for p-ADA, the TICT band initially at 628 nm was bathochromically shifted upto 648 nm with a concomitant decrease in the emission intensity. When temperature was increased from 25 °C to 75 °C, the TICT band initially at 628 nm was blue shifted upto 613 nm with concomitant decrease in the emission intensity (Figure 7d). Compound p-AD in 2MeTHF showed similar behaviour in the temperature range 25 °C to -15 °C where the TICT band at 631 nm at 25 °C was red-shifted to 646 nm and decreasing intensities upon decreasing temperature. Upon increasing temperatures for p-AD in 2MeTHF (Figures S8, S9) however, the TICT band at 631 nm at 25 °C was blue shifted upto 613 nm with decreasing intensities.



Figure 7. Temperature dependent fluorescence emission spectra of triad p-ADA in a) DCM; b) THF; c) Toluene and d) 2MeTHF.





Cryogenic temperature (-196 °C) fluorescence was measured for **p-AD** and **p-ADA** in 2MeTHF in a cryogenic setup and the emission centred at ~ 519 nm and ~ 523 nm were observed for **p-AD** and **p-ADA** respectively (Figure 8), whereas any emission from the TICT state were completely absent for both compounds.

#### **Ratiometric Temperature Sensing Analysis**

Ratiometric analysis of temperature dependent emission is possible when one emission band changes with temperature while the other band remains unchanged or changes negligibly with temperature.<sup>[1]</sup> The plot of ratio of intensities with temperature can be fitted with linear,<sup>[28,49,66]</sup> exponential,<sup>[51]</sup> or polynomial functions<sup>[52]</sup> to obtain temperature coefficients and sensitivities of such molecular thermometers. Since temperature dependent emission of p-AD and p-ADA in different solvents revealed pronounced temperature dependent intensity changes in the TICT band (I<sub>2</sub>) while the LE/BDT emission band remained relatively unchanged (I1), ratiometric analyses of these data were performed. The ratiometric analyses (i.e., plot of  $I_1/I_1+I_2$  vs. T) revealed unique temperature sensing behaviour for **p-AD** and p-ADA in different solvents. The ratio of intensities with temperature plot for p-AD in THF, CHCl<sub>3</sub> and 2MeTHF were fitted with exponential functions with goodness of fit R<sup>2</sup> values of 0.98-0.99 (Figures S12, S13, S8 and S9 and Table S8). The internal sensitivities were obtained by differentiation of the fitted plots of intensity ratio vs temperature<sup>[51]</sup> and internal sensitivities in the range of 0.6 % °C<sup>-1</sup> to -0.8 % °C<sup>-1</sup> was obtained in various solvents as tabulated in Table S8. The plot of intensity ratio for p-AD in 2MeTHF with temperature was fitted in two stages, a lower temperature range (-15 °C to 25 °C) and a higher temperature range (25 °C to 75 °C). In the lower temperature range, a negative temperature coefficient with internal sensitivities of -0.05 % °C<sup>-1</sup> to -0.67% °C<sup>-1</sup> was obtained (Figure S9, Table S8). In the higher temperature range however, a positive temperature coefficient with internal sensitivities from 0.07 %  $^{\circ}C^{-1}$  to 0.6 %  $^{\circ}C^{-1}$  was obtained (Figure S8, Table S8). The plot of intensity ratio of p-AD in toluene with respect to temperature could be fitted with a linear function with goodness of fit (R<sup>2</sup>) of 0.97 (Figure S14) with positive temperature coefficient, slope of 0.0017 and thus a temperature sensitivity of 0.17 % °C<sup>-1</sup>. The fitted equation obtained (for **p-AD** in toluene) was:

$$(I_{431}/I_{431} + I_{532}) = 0.0017 T + 0.1953$$

where,  $I_{431}$  and  $I_{532}$  are the fluorescence intensities at emission wavelengths of 431 nm and 532 nm, respectively.

For **p-ADA** rotor, the ratio of emission intensities,  $I_1/I_1+I_2$  was plotted with respect to temperature in different solvents and the data in toluene, THF, DCM and CHCI<sub>3</sub> were fitted with exponential functions<sup>[51]</sup> with goodness of fit (R<sup>2</sup>) 0.99-0.93 (Figures S15-S18). The plots for the internal sensitivities are

### WILEY-VCH

presented in Table S5 and sensitivities in the range of 0.16 %  $^{\circ}C^{-1}$  to -1.88 %  $^{\circ}C^{-1}$  were obtained. Notably, the temperature coefficients in THF, CHCl<sub>3</sub>, DCM were negative while that in toluene was positive. For **p-ADA** in DCM, the plot of intensity ratio with temperature was fitted with a linear function with goodness of fit (R<sup>2</sup>) was 0.93, a negative temperature coefficient and sensitivity of -0.43 %  $^{\circ}C^{-1}$ . The fitted equation (for **p-ADA** in DCM) obtained was:

#### $(I_{431}/I_{431} + I_{677}) = -0.0043 T + 0.5937$

where,  $I_{431}$  and  $I_{667}$  are the fluorescence intensities at emission wavelengths of 431 nm and 677 nm, respectively. The temperature dependent emission of p-ADA in 2MeTHF in the decreasing temperature range (25°C to -15°C) was fitted with exponential function (Figure S10, Table S8) while the data in the increasing temperature range (25°C to 75°C) was fitted with linear plot with R<sup>2</sup> value of 0.93 (Figure S11), positive temperature coefficient and slope of 0.0016, thus a sensitivity of 0.16 % °C<sup>-1</sup>. Temperature dependent fluorescence study was performed also for m-ADA in CHCl<sub>3</sub> and Toluene. Interestingly, while the emission in toluene was centred around 525 nm that increased upon reducing the temperature, the emission in CHCI<sub>3</sub> was characterized by a weak broad band at ~ 660 nm that indicated aggregation as discussed above. This aggregation band upon reduction in temperature increased in intensity owing to reduced intramolecular rotation and reduced conformational freedom at lower temperatures. The temperature dependent emission for m-ADA in CHCl<sub>3</sub> showed good ratiometric behavior where the ratio of intensities with temperature plot could be fitted with a linear function with a goodness of fit (R<sup>2</sup>) value of 0.98 (Figure S19). The fitted equation obtained (for m-ADA in CHCl<sub>3</sub>) was:

#### $(I_{435}/I_{435}+I_{662}) = -0.0041 T + 0.6562$

where,  $I_{435}$  and  $I_{662}$  are the fluorescence intensities at emission wavelengths of 435 nm and 662 nm respectively. The fitted plot had a negative temperature coefficient and slope of -0.0041, thus a temperature sensitivity of 0.41 % °C<sup>-1</sup>. It however showed a positive temperature coefficient in toluene (Figure S20) with sensitivity of 0.21 % °C<sup>-1</sup>. Compared to **m-ADA**, dyad counterpart **m-AD** was not much temperature responsive in variety of solvents when compared to **p-AD** or **m-ADA**.

Thus, to summarize from ratiometric temperature analyses, all three rotors p-AD, p-ADA, and m-ADA showed positive temperature coefficient in toluene. In these cases, the emission that was monitored was predominantly the LE/BODIPY emission. Moreover, p-ADA and p-AD showed positive temperature coefficient in 2MeTHF in the temperature range 25 °C to 75 °C. The small sensitivities obtained for p-AD, p-ADA and m-ADA indicate that a range of temperature can be measured precisely using these molecules. Rotors p-AD and p-ADA also showed negative temperature coefficients in THF,  $\ensuremath{\mathsf{CHCl}}_3$  and in the lower temperature range in 2MeTHF. The summary of temperature behaviour of emission of these rotors in various solvents have been tabulated in Table S9. Such studies indicate the utility of these dyad and triad rotors as molecular thermometers for temperature of microenvironments sensina upto the macroscopic scale in the physiological temperature range.

#### Viscosity Induced Fluorescence Enhancement

Viscosity dependent emission were measured for dyads **p-AD** and **m-AD** and triad **m-ADA** in a series of mixtures of MeOH and glycerol (v/v) to understand the viscosity effect on

conformations of these molecules in the excited state. The fluorescence intensity increased with increasing the viscosity of solvent using a glycerol/methanol mixture for all compounds. The solvent viscosity was varied from 100/0 to 10/90 MeOH/glycerol (0.6 cP to 454 cP) v/v.[49] Restricting the rotation of molecular rotors in a viscous medium enhances fluorescence intensity. Since glycerol is more polar than MeOH, upon increasing the percentage of glycerol, there will be an overall increase in the solvent polarity. However, the viscosity of glycerol overrules the polarity increment effect and the viscosity restricts the intramolecular rotation thereby leading to LE emission exclusively. The restriction of the intramolecular rotation in the viscous medium hinders the TICT deactivation pathway and thus the TICT band or the band in the longer wavelength region was completely absent in case of the dyads p-AD and m-AD (Figure 9a, b) and in triads p-ADA and m-ADA (Figure 9c, d). In case of p-AD, the peaks (at ~ 425 nm and ~ 520 nm) did not shift upon increasing the percentage of glycerol but the intensities of the peaks as well as the spectral shape changed upon increasing percentage of glycerol.

Similar effect was observed in case of **m-AD** where upon increasing the percentage of glycerol, the fluorescence intensity drastically increased almost five times from initial value (Figure 9b).



Figure 9. Viscosity dependent fluorescence emission spectra of dyads a) p-AD; b) m-AD; and triads c) p-ADA; d) m-ADA.

While in **p-ADA**, only the emission from the LE state and the BDT was observed (Figure 9c) and in **m-ADA** the peaks were slightly blue shifted with spectral broadening at 90/10 (v/v) of glycerol/MeOH mixture (Figure 9d). For all compounds, solvent polarity had no effect and the blue shift observed was primarily attributed to the rigidification of the molecular geometry. In order to quantitatively assess the viscosity sensitivity of the four molecules, viscosity dependent emission was expressed using Förster Hoffmann theory<sup>[10,11]</sup>:

#### $\log (I/I_0) = C + x \log \eta$

where,  $I_0$  and I are the emission intensities at the initial viscosity i.e., in 100 % MeOH and in glycerol/ MeOH mixtures with increasing glycerol percentage respectively.

The viscosity of the medium is given by  $\eta$ , C is the experimental temperature and concentration dependent constant and x is the viscosity sensitivity of the molecular rotors. According to this analysis (Figure S21, Table S10), **p-AD**, **m-AD**, **p-ADA** and **m**-

WILEY-VCH

ADA showed viscosity sensitivity (x) of 0.09, 0.23, 0.12, 0.31 respectively. Typical values of slopes (x) for rotors vary from 0.1 to 1.4 for different rotors.<sup>[24,67]</sup> Thus, among four compounds, m-ADA is most sensitive to viscosity and shows the best viscosity sensing (x = 0.31) characteristics.

Furthermore, temperature effect on a particular viscosity was also investigated for all compounds. A solution of glycerol/ MeOH mixture 70/30 (v/v) (104 cP) of p-AD, p-ADA, m-AD and m-ADA were subjected to temperature dependent fluorescence measurement. The fluorescence intensity decreased on increasing the temperature (Figure S22). It is reported that at higher temperatures, viscosity and polarity tend to decrease dramatically.<sup>[11,68]</sup> Reduction in fluorescence intensities upon increasing the temperature is indicative of reduced viscosity and thus higher molecular motion and thus rapid non-radiative deactivation. Furthermore, no (hypsochromic) shifts in peak positions were observed upon increasing the temperature indicating that solvent polarity did not change significantly. The decrease in fluorescence intensity was thus predominantly due to viscosity effect at variable temperatures.

### Conclusions

Regioisomeric acceptor-donor (AD) molecular dyads p-AD and m-AD and triad m-ADA were synthesized and characterized in this work where dyads p-AD and m-AD and triad m-ADA contained BODIPY and BDT as electron acceptor and donor respectively. In all compounds, the D and A moieties are electronically decoupled by a phenyl spacer, either through a para coupling or through a meta coupling. Regioisomerism had a profound impact on the photophysical characteristics of dvads p-AD and m-AD where, dyad p-AD was multiple emissive with a prominent TICT band at 654 nm and a large Stokes shift of ~ 150 nm. Positive fluorescence solvatochromism and AIE was observed for p-AD. The meta counterpart m-AD however, showed an extremely weak TICT type emission owing to the weaker meta phenyl coupling. The meta triad m-ADA showed well-defined aggregation in solution evident from emission studies. Interestingly, fluorescence of dyad m-AD (in 10/90 v/v THF/water) revealed a near white light emission with CIE chromaticity coordinates (x, y) of (0.32, 0.29). Furthermore, fluorescence of p-AD in THF at 0 °C also showed a near white light emission with chromaticity coordinates (x, y) of (0.34, 0.27). Notably, all compounds showed temperature tunable and viscosity dependent emission changes. A ratiometric analysis of temperature dependent fluorescence of p-AD, p-ADA and m-ADA in different solvents showed that temperature sensitivities in the range of 0.21 % °C<sup>-1</sup> to -1.88 % °C<sup>-1</sup>. Moreover, p-AD, p-ADA and m-ADA showed positive temperature coefficients in toluene while p-AD and p-ADA showed negative temperature coefficients in THF and CHCl<sub>3</sub>. By utilizing the LE and the TICT emissions (through variation of solvent), it was thus possible to achieve ratiometric sensors with either positive or negative temperature coefficients. A range of temperature can thus be measured precisely using these rotors and can serve as precise molecular thermometers for temperature sensina of microenvironments. Viscosity dependence of fluorescence intensities was analysed for all rotors where viscosity sensitivities in the range of 0.09-0.31 were obtained, with m-ADA being the best viscosity sensor (x = 0.31) in the series. At present, efforts to understand the molecular level picture governing the tunable emission properties of these rotors as well as design of newer molecules with improved properties are underway in our group.

### Acknowledgements

The financial support from Department of Science and Technology (DST), New Delhi (DST/TM/SERI/FR/162) and IISER Mohali is gratefully acknowledged. The authors thank central (NMR and MS) and departmental facilities of IISERM. A.P.R. thanks DST-INSPIRE for BS-MS fellowship, S.S. and N.P.T. thank IISERM for Ph.D. fellowships. We thank Dr. Kamalakannan Kailasam, Institute of Nano Science and Technology, Mohali for providing access to temperature dependent UV/Vis facility. We extend our sincere gratitude to Mr. Mayank Saraswat for insightful discussion and help regarding the FMO composition analysis. We thank Dr. Sugumar Venkataramani and Dr. Arijit K. De for fruitful discussion regarding some of the photophysical studies.

Keywords: BODIPY · Regioisomer · Ratiometric temperature sensor • Twisted intramolecular charge transfer (TICT) • Viscosity sensor.

#### References

- [1] X. D. Wang, O. S. Wolfbeis and R. J. Meier, Chem. Soc. Rev., 2013, 42, 7834–7869.
- [2] L. R. Bradshaw, D. R. Gamelin and E. J. McLaurin, Chem. Mater., 2013, 25, 1283-1292.
- X. Huang, J. Song, B. C. Yung, X. Huang, Y. Xiong and X. Chen, Chem. Soc. Rev., 2018, 47, 2873–2920. [3]
- S. Sasaki, G. P. C. Drummen and G. I. Konishi, J. Mater. Chem. C, [4] 2016, 4, 2731-2743
- G. S. Kottas, L. I. Clarke, D. Horinek and J. Michl, Chem. Rev., [5] 2005, 105, 1281-1376.
- [6] Z. R. Grabowski, K. Rotkiewicz and W. Rettig, Chem. Rev., 2003, 103. 3899-4032.
- R. Hu, E. Lager, J. Liu, J. W. Y. Lam, H. H. Y. Sung, I. D. Williams, [7] Y. Zhong and K. S. Wong, J. Phys. Chem. C., 2009, 113, 15845-15853.
- D. Liese and G. Haberhauer, Isr. J. Chem., 2018, 58, 813-826. [8] [9] M. M. A. Mazza and F. M. Raymo, J. Mater. Chem. C, 2019, 7,
- 5333-5342. [10] D. Su, C. L. Teoh, L. Wang, X. Liu and Y. T. Chang, Chem. Soc.
- Rev., 2017, 46, 4833–4844. A. Vyšniauskas and M. K. Kuimova, Int. Rev. Phys. Chem., 2018, [11]
- 37, 259-285.
- [12] C. Zhong, Phys. Chem. Chem. Phys., 2015, 17, 9248-9257.
- D. Li, W. Hu, J. Wang, Q. Zhang, X. M. Cao, X. Ma and H. Tian, [13] Chem. Sci., 2018, 9, 5709–5715.
- [14] S. Mukherjee and P. Thilagar, Dye. Pigment., 2014, 110, 2–27.
- J. Mei, Y. Hong, J. W. Y. Lam, A. Qin, Y. Tang and B. Z. Tang, Adv. Mater., 2014, 26, 5429–5479. [15]
- Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Soc. Rev.*, **2011**, *40*, 5361–5388. [16]
- Y. Gong, Y. Zhang, W. Z. Yuan, J. Z. Sun and Y. Zhang, *J. Phys. Chem. C*, **2014**, *118*, 10998–11005. [17]
- [18] M. A. Haidekker and E. A. Theodorakis, Org. Biomol. Chem., 2007, 5, 1669-1678.
- [19] M. K. Kuimova, Phys. Chem. Chem. Phys., 2012, 14, 12671-12686. R. Kotani, H. Sotome, H. Okajima, S. Yokoyama, Y. Nakaike, A. Kashiwagi, C. Mori, Y. Nakada, S. Yamaguchi, A. Osuka, A. [20]
  - Sakamoto, H. Miyasaka and S. Saito, J. Mater. Chem. C, 2017, 5, 5248-5256
- [21] A. J. Thompson, T. W. Herling, M. Kubánková, A. Vyšniauskas, T. P. J. Knowles and M. K. Kuimova, J. Phys. Chem. B, 2015, 119, 10170-10179.
- M. Qurashi, M. K. Kuimova, A. Vyšniauskas, D. Ding, M. Balaz, H. L. Anderson and I. Boczarow, *Chem. A Eur. J.*, **2017**, *23*, 11010. [22]
- A. Vyšniauskas, I. López-Duarte, N. Duchemin, T. T. Vu, Y. Wu, E. [23] M. Budynina, Y. A. Volkova, E. Peña Cabrera, D. E. Ramírez-Ornelas and M. K. Kuimova, Phys. Chem. Chem. Phys., 2017, 19, 25252-25259.
- [24] S. L. Raut, J. D. Kimball, R. Fudala, I. Bora, R. Chib, H. Jaafari, M. K. Castillo, N. W. Smith, I. Gryczynski, S. V. Dzyuba and Z. Gryczynski, *Phys. Chem. Chem. Phys.*, **2016**, *18*, 4535–4540.

### WILEY-VCH

- Z. Yang, Y. He, J. H. Lee, N. Park, M. Suh, W. S. Chae, J. Cao, X. [25] Peng, H. Jung, C. Kang and J. S. Kim, J. Am. Chem. Soc., 2013, 135, 9181–9185.
- [26] M. K. Kuimova, G. Yahioglu, J. A. Levitt and K. Suhling, J. Am. Chem. Soc., 2008, 130, 6672-6673.
- Y. V. Zatsikha, N. O. Didukh, R. K. Swedin, V. P. Yakubovskyi, T. S. [27] Blesener, A. T. Healy, D. E. Herbert, D. A. Blank, V. N. Nemykin and Y. P. Kovtun, *Org. Lett.*, **2019**, *21*, 5713–5718.
   W. Chi, W. Yin, Q. Qi, Q. Qiao, Y. Lin, Z. Zhu, S. Vijayan, M.
- [28] Hashimoto, G. Udayakumar, Z. Xu and X. Liu, Mater. Chem. Front., 2017, 1, 2383-2390.
- C. Cao, X. Liu, Q. Qiao, M. Zhao, W. Yin, D. Mao, H. Zhang and Z. [29] Xu, Chem. Commun., 2014, 50, 15811-15814.
- [30] T. Xia, L. Wang, Y. Qu, Y. Rui, J. Cao, Y. Hu, J. Yang, J. Wu and J. Xu, *J. Mater. Chem. C*, **2016**, *4*, 5696–5701. S. C. Lee, J. Heo, J. W. Ryu, C. L. Lee, S. Kim, J. S. Tae, B. O.
- [31] Rhee, S. W. Kim and O. P. Kwon, Chem. Commun., 2016, 52, 13695–13698.
- [32] F. Liu, T. Wu, J. Cao, S. Cui, Z. Yang, X. Qiang, S. Sun, F. Song, J Fan, J. Wang and X. Peng, *Chem. - A Eur. J.*, **2013**, *19*, 1548–1553. X. Peng, Z. Yang, J. Wang, J. Fan, Y. He, F. Song, B. Wang, S. Sun, J. Qu, J. Qi and M. Yan, *J. Am. Chem. Soc.*, **2011**, *133*, 6626–6635. [33]
- L. Wang, Y. Xiao, W. Tian and L. Deng, J. Am. Chem. Soc., 2013, 135, 2903–2906. [34] Roopa, N. Kumar, V. Bhalla and M. Kumar, Chem. Commun., 2015, [35]
- 51, 15614-15628. A. Mustafic, H. M. Huang, E. A. Theodorakis and M. A. Haidekker, J.
- [36] Fluoresc., 2010, 20, 1087-1098. A. Loudet and K. Burgess, Chem. Rev., 2007, 107, 4891-4932. [37]
- [38] G. Ulrich, R. Ziessel and A. Harriman, Angew. Chemie - Int. Ed., 2008. 47. 1184-1201.
- N. Boens, V. Leen and W. Dehaen, Chem. Soc. Rev., 2012, 41, [39] 1130-1172.
- [40] S. Cherumukkil, B. Vedhanarayanan, G. Das, V. K. Praveen and A. Ajayaghosh, Bull. Chem. Soc. Jpn., 2018, 91, 100-120.
- [41] D. Okada, T. Nakamura, D. Braam, T. D. Dao, S. Ishii, T. Nagao, A. Lorke, T. Nabeshima and Y. Yamamoto, ACS Nano, 2016, 10, 7058-7063.
- S. Cherumukkil, S. Ghosh, V. K. Praveen and A. Ajayaghosh, Chem. [42] Sci., 2017, 8, 5644-5649.
- D. Tian, F. Qi, H. Ma, X. Wang, Y. Pan, R. Chen, Z. Shen, Z. Liu, L. [43] Huang and W. Huang, Nat. Commun., 2018, 9, 1-9.
- [44] T. T. Vu, R. Méallet-Renault, G. Clavier, B. A. Trofimov and M. K. Kuimova, J. Mater. Chem. C, 2016, 4, 2828-2833.
- [45]
- G. P. C. Drummen, *Molecules*, 2012, *17*, 14067–14090.
   H. C. Ishikawa-Ankerhold, R. Ankerhold and G. P. C. Drummen, *Molecules*, 2012, *17*, 4047–4132.
   K. Xiong, F. Huo, Y. Zhang, Y. Wen and C. Yin, *Anal. Methods* 2019, [46]
- [47] 11, 1751-1756.
- [48] F. Hammerer, G. Garcia, P. Charles, A. Sourdon, S. Achelle, M. P. Teulade-Fichou and P. Maillard, Chem. Commun., 2014, 50, 9529-

- 9532
- [49] B. Sk, S. Khodia and A. Patra, Chem. Commun., 2018, 54, 1786-1789.
- S. Liu, X. Zhou, H. Zhang, H. Ou, J. W. Y. Lam, Y. Liu, L. Shi, D. [50] Ding and B. Z. Tang, *J. Am. Chem. Soc.*, **2019**, *141*, 5359–5368. Y. Guo, S. Gu, X. Feng, J. Wang, H. Li, T. Han, Y. Dong, X. Jiang, T.
- [51]
- D. James and B. Wang, *Chem. Sci.*, **2014**, *5*, 4388–4393. Q. Fang, J. Li, S. Li, R. Duan, S. Wang, Y. Yi, X. Guo, Y. Qian, W. Huang and G. Yang, *Chem. Commun.*, **2017**, *53*, 5702–5705. [52]
- S. Sengupta and U. K. Pandey, Org. Biomol. Chem., 2018, 16, [53] 2033-2038.
- C. K. Lin, C. Prabhakar and J. S. Yang, J. Phys. Chem. A, 2011, [54] 115, 3233-3242.
- [55] M. V. Bohnwagner, I. Burghardt and A. Dreuw, Phys. Chem. Chem. Phys., 2017, 19, 13951-13959.
- S. Sasaki, K. Igawa and G. I. Konishi, J. Mater. Chem. C, 2015, 3, [56] 5940-5950.
- [57] R. Liu, H. Ran, Z. Zhao, X. Yang, J. Zhang, L. Chen, H. Sun and J. Y. Hu, ACS Omega, 2018, 3, 5866-5875.
- [58] R. Ghosh and D. K. Palit, J. Phys. Chem. A, 2015, 119, 11128-11137.
- [59] A. K. Rawat and S. M. S. Chauhan, Der Pharma Chem., 2014, 6, 316-322
- A. J. F. N. Sobral, N. G. C. L. Rebanda, M. Da Silva, S. H. Lampreia. [60] M. Ramos Silva, A. Matos Beja, J. A. Paixão and A. M. D. A. Rocha Gonsalves, Tetrahedron Lett., 2003, 44, 3971-3973.
- [61] G. Tarafdar, S. Sengupta, U. K. Pandey and P. C. Ramamurthy, Photovoltaics Specialist Conference (PVSC) 2016 IEEE 43rd, 1664-1669.
- Xie, C. Chen, S. Xu, J. Li, Y. Zhang, S. Liu, J. Xu and Z. Chi, Angew. Chemie Int. Ed., 2015, 54, 7181–7184.
  Y. Yang, M. Lowry, C. M. Schowalter, S. O. Fakayode, J. O. Escobedo, X. Xu, H. Zhang, T. J. Jensen, F. R. Fronczek, I. M. [62]
- [63] Warner and R. M. Strongin, J. Am. Chem. Soc., 2006, 128, 14081-14092.
- [64] Z. He, W. Zhao, J. W. Y. Lam, Q. Peng, H. Ma, G. Liang, Z. Shuai
- [65]
- Her, W. Zhao, J. W. T. Lain, Q. Perig, H. Ma, G. Llaig, Z. Shuar and B. Z. Tang, *Nat. Commun.*, **2017**, *8*, 1–7.
   Q. Fang, J. Li, S. Li, R. Duan, S. Wang, Y. Yi, X. Guo, Y. Qian, W. Huang and G. Yang, *Chem. Commun.*, **2017**, *53*, 5702–5705.
   J. Feng, K. Tian, D. Hu, S. Wang, S. Li, Y. Zeng, Y. Li and G. Yang, *Angew. Chemie Int. Ed.*, **2011**, *50*, 8072–8076.
   M. Aldelahles end Ed. The detablish of Ed. Fund. [66]
- M. A. Haidekker and E. A. Theodorakis, J. Biol. Eng., 2010, 4, 1-14. [67] [68] A. Vyšniauskas, M. Qurashi, N. Gallop, M. Balaz, H. L. Anderson and M. K. Kuimova, Chem. Sci., 2015, 6, 5773-5778.

### WILEY-VCH

# **FULL PAPER**

**Entry for the Table of Contents** (Please choose one layout) Layout 1:

# FULL PAPER

Molecular Sensors: Regioisomeric BODIPY-Benzodithiophene dyads and triads show either twisted intramolecular charge transfer (TICT) with red emission or aggregation in solution. These rotors exhibit tunable emission, red pronounced temperature and viscosity sensing and near-white light emission that are promising for bioimaging and sensing applications.



Aswathy P. R., S. Sharma, N. P. Tripathi, S. Sengupta\*

Page No. – Page No.

Regioisomeric BODIPY-Benzodithiophene Dyads and Triads with Tunable Red Emission as Ratiometric Temperature and Viscosity Sensors.