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Trifluoroacetic Acid Prompted Unexpected Visible to NIR Switching of Ketoenamine-substituted Triphenylamines

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Abstract

We report a trifluoroacetic acid (TFA) induced absorption shift of π-extended ketoenamine-substituted triphenylamines from blue (420-450 nm) to near-infrared (NIR) (1020-1080 nm) spectral region. The phenomenon is highly specific to TFA while only mild (to ~580 nm) shift is observed in other studied acids (stronger or weaker Bronsted and Lewis acid). The unexpected NIR absorption originates from the radical cation species formed upon electron transfer from trifluoroacetate to the protonated triphenylamine. The formation of radical cation is confirmed by electron paramagnetic resonance (EPR) spectroscopy.

Introduction

π-Conjugated molecules with a very low optical gap (≤1 eV) are of interest due to their potential for various applications including printing, information storage and counterfeit protection, photovoltaics, (bio)imaging, photothermal therapy, telecommunications, etc.[1,2] Current approaches were developed towards the synthesis of NIR absorbing molecules in the form of π-extended polycyclic aromatics,[3–5] cyanine dyes[6–10] and 'push-pull' molecular and polymer structures incorporating strong electron-donor (D) and electron-acceptor (A) moieties.[11–15] Tailoring the D-A interactions in a molecule/polymer has proven a versatile approach to bandgap engineering.[16–20] Although such D-A interactions readily give rise to low-bandgap chromophores with NIR absorption, achieving them requires challenging multi-step synthesis and the resulting materials often have limited environmental stability.[21,22]

Stimuli-responsive photo-functional materials are of interest because of their ability to reversibly modulate the electronic properties without synthetic alterations. In particular, proton-responsive (halochromic) materials find applications such as pH sensors,[23–27] electrochromic textiles,[28,29] fluorescent switches,[30–32] photovoltaics[33,34] and light emitting diodes.[35] Halochromic properties have been demonstrated for a wide variety of π-conjugated molecules including benzothiadiazole,[36] amino-substituted oligothiophenes,[37] polycyclic aza-aromatics,[38–40] perylene diimide[41] and also a few electron-rich triarylamine derivatives.[42–47] Generally, the spectral shift in these materials does not exceed ~100-300 nm and the absorption band most often lies within the visible region, while NIR halochromic materials are rare. Azulene-based conjugated oligomers[48–50] and polymers[51,52] are the best known protonation-induced visible (~500 nm) to NIR absorption switching materials (~1500 nm) and by fine-tuning the molecular structures, the maxima can be extended up to 2500 nm. More recently, Sessler *et al*[53] reported pronounced halochromic behaviour for quinoxaline annulated tetrathiafulvalene (TTF) derivatives with the absorption band shifting from ~450 nm to ~1250

nm. Also, hydroxy-substituted perylene diimides[54] display base-induced NIR absorption at 1185 nm.

Herein, we report unexpected NIR absorption of triphenylamine-ketoenamine donor-acceptor compounds induced by trifluoroacetic acid (TFA). The process is fully reversible and shifts the absorption from visible (~400 nm) to NIR (~1050 nm). The behaviour is specific to TFA while all other tested acids induce only a mild (~100 nm) redshift.

Results and Discussion

Synthesis, DFT and electrochemistry:

The ketoenamine substituted triarylamines **1-3** were prepared *via* Michael addition-elimination[55] of *tris*-(*p*-aminophenyl)amine **7** to ketoenols **4-6** in 76-79% yields (Scheme 1). Precursors **4-6** are easily accessible from corresponding acetophenones *via* formylation with ethyl formate in the presence of a base (*t*-BuOK). **1-3** were obtained as yellow powders that are readily soluble in common organic solvents. The density functional theory (DFT) (B3LYP 6-31G(d)) optimized molecular structures of **1-3** reveal a C3-symmetric propeller conformation akin to that of the parent triphenylamine (Fig. 1a). Each of their three arms is nearly planar (minor twist of ~13°), enforced by the intramolecular hydrogen bonding of ketoenamine (NH…O ~1.8 Å) which facilitates π-delocalization over the entire molecule. The DFT deduced HOMO-LUMO gaps follow an order of **3** (2.59 eV) < **1** (2.94 eV) < **2** (3.01 eV) (Fig. 1b). The relatively narrow bandgap of compound **3** is attributed to increased donor-acceptor interactions due to the electron-withdrawing cyano group. In the similar lines, the TD-DFT predicts redshift in the absorption spectrum for **3** compared to **1-2** and the trend closely matches to the solution state spectra (vide infra, Fig. S1). In cyclic voltammetry, **1-3** exhibit two partially reversible oxidation waves and their first oxidation potentials [**3** (0.83 V *vs* SCE > **1** (0.79 V) > **2** (0.75 V)] are in line with the expected electronic effects of the substituents (Fig. S2).
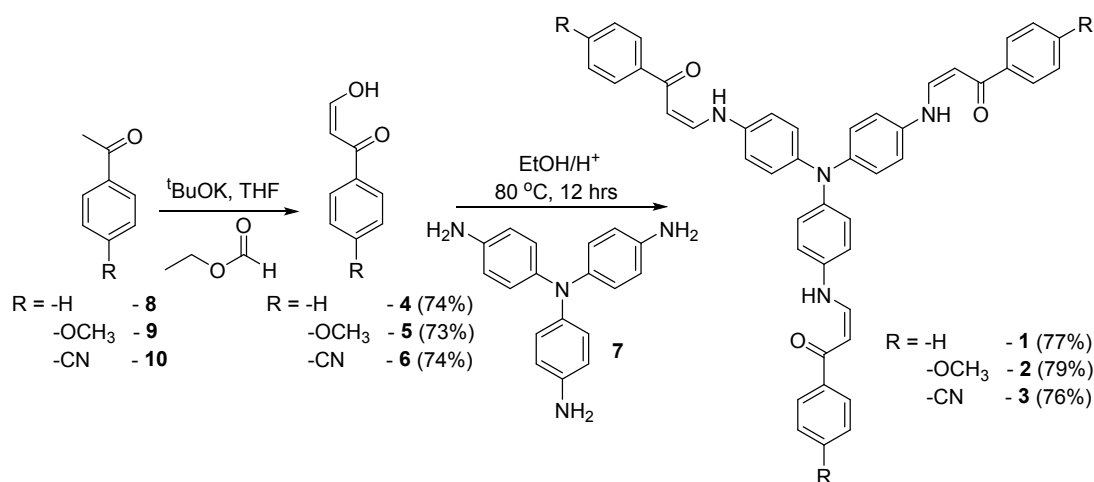
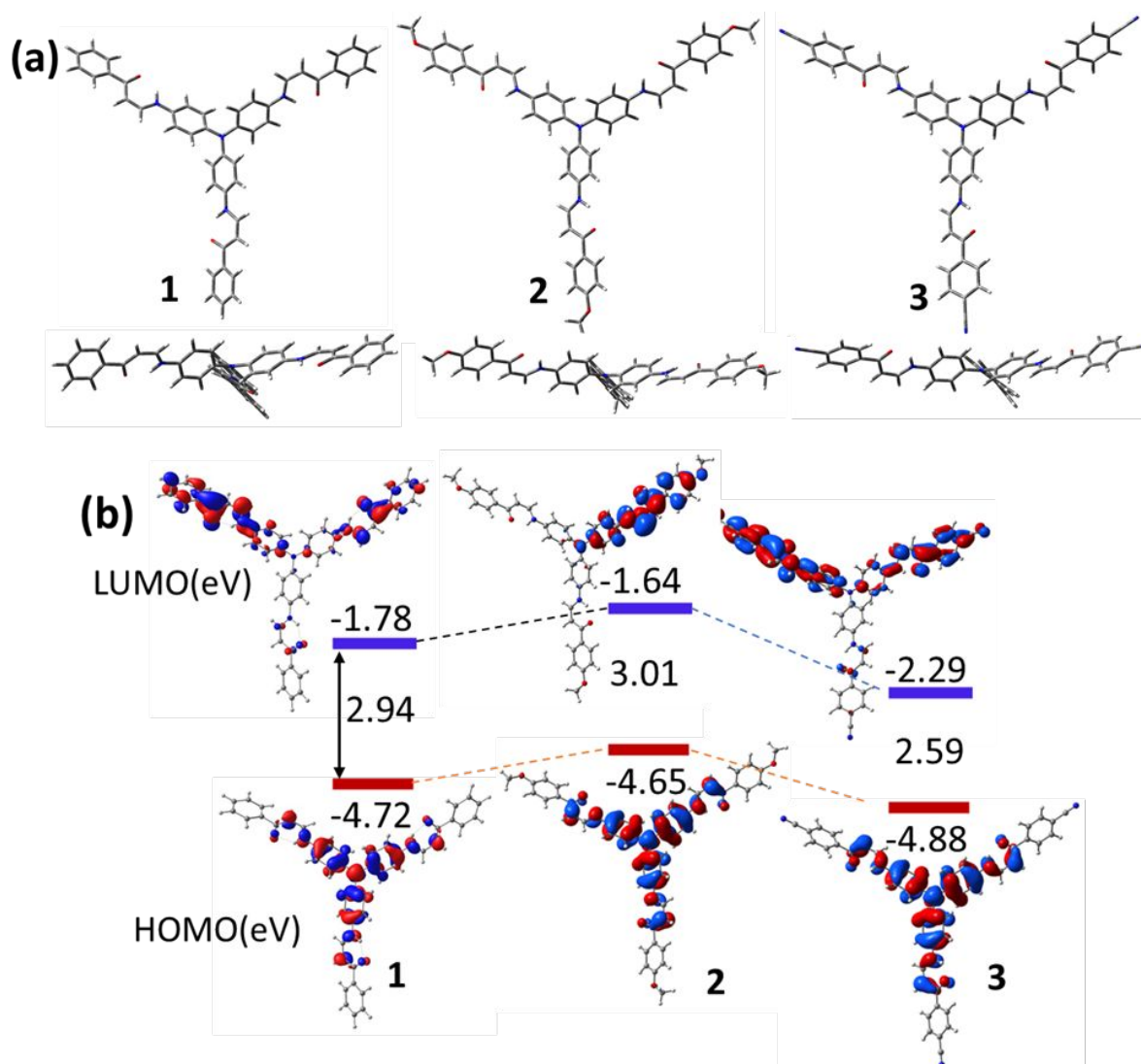**Scheme 1:** Synthesis of compounds **1-3**.

Fig. 1 DFT-optimized (a) structures (b) HOMO/LUMO frontier orbital topologies and their HOMO-LUMO (H-L) gaps of **1-3**. [B3LYP/6-31G(d), CPCM solvent model; chloroform]

Photophysics:

Dichloromethane (DCM) solutions of **1-3** show the longest wavelength absorption bands at

λ_{max} = 423, 426 and 453 nm, respectively (Fig. 2a). As DFT predicted, **3** exhibits red shifted

absorption due to the electron-withdrawing cyano group. The compounds **1-3** show only a

weak fluorescence with fluorescence quantum yields of ~1-2% (Table 1 and S1), likely due to

intramolecular charge transfer (ICT) (Fig. 2a and Fig. S3-S5). The solvent sensitive emission

(broad, redshifted and diminishing emission in polar solvents) of **1-3** indicates the existence of

ICT. This is further supported by DFT predicted HOMO and LUMO electronic distributions

which shows that the HOMO is populated on the central TPA unit and the LUMO on the

peripheral aryl ketoenamine (Fig. 1b). On the other hands, the UV-Vis spectra of **1-3** in solvents

of different polarity (toluene to DMF) showed only a small solvatochromic shift (<5 nm, Fig.

S6-S8). However, striking spectral changes were noticed when solutions of **1-3** were treated

with TFA (pK$_a$ =0.23). Upon addition of TFA, the absorption band of **1** at λ_{max} = 423 nm

progressively diminishes, and three new bands appear at λ_{max} = 382, 449 and 1053 nm. Similar

spectral changes were also observed with **2** and **3** in the presence of TFA, showing

characteristic NIR absorption maxima at 1083 and 1024 nm, respectively (Fig. 2d). This NIR

absorption closely matches the absorption of ketoenamine radical-cation,[55] prepared by a (well-

established[56] oxidation with iodine (Fig. 3a). Further, the TD-DFT calculations of the cation

radical **1•+** predict a similar NIR absorption (1080 nm, Fig. 5c) which corresponds to

HOMO→LUMO transition. Thus, we suspect that compounds **1-3** in TFA undergo an electron

transfer to form an open-shell radical-cation. Upon subsequent addition of triethylamine (Et$_3$N)

to the protonated compound, the NIR absorption band disappears, and the original spectral

features of neutral compounds fully restore. The neutral compounds can be recovered after

such TFA/Et$_3$N treatment cycle in near-quantitative yields (Fig. 3b). On the other hand, the

Table 1: Optical, electrochemical and DFT data of **1-3**

Product	[a]Absorption			Fluorescence	[d]Cyclic Voltammetry	[e]DFT		
	λ_{max} /nm	[b]Optical gap /eV	[c]ε /cm^{-1} M^{-1}	λ_{em} /nm (φ_f)	E_{ox} /V vs Ferrocene	HOMO /eV	LUMO /eV	E_g /eV
1	423	2.45	2.3 x 10^{-5}	578 (0.1%)	0.79	-4.72	-1.78	2.94
2	426	2.46	1.7 x 10^{-5}	563 (1.5%)	0.75	-4.65	-1.64	3.01
3	453	2.27	1.5 x 10^{-5}	604 (1.6%)	0.83	-4.48	-2.29	2.59

[a]Measured in 10^{-5} M CHCl$_3$ solution, [b]optical gap = 1240/λ_{max}, [c]ε = molar extinction coefficient, [d] performed using tetrabutylammonium perchlorate as electrolyte, [e]optimized using B3LYP/6-31G(d), CPCM solvent model; chloroform.
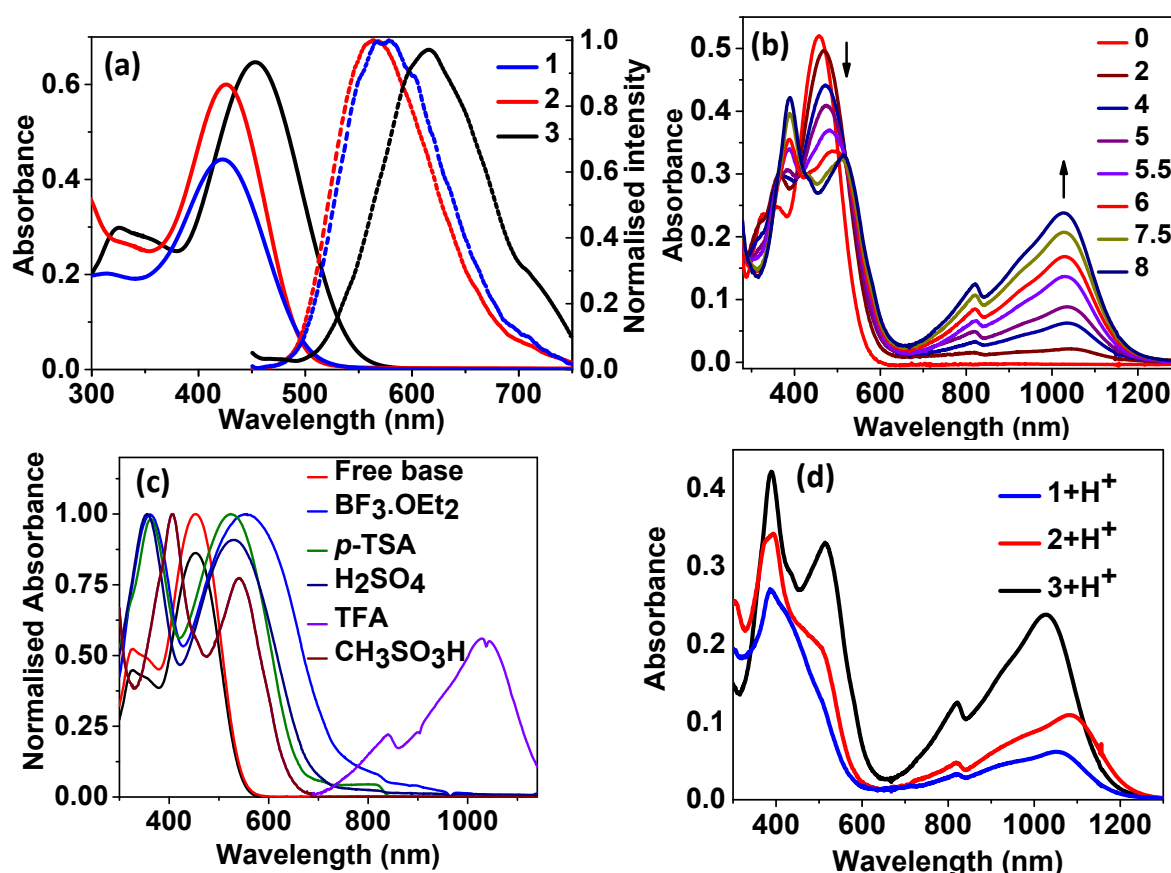

Fig. 2 (a) Absorption and emission spectra of compounds **1–3** in CHCl$_3$; (b) spectral changes of CHCl$_3$ solution of **3** upon addition of various amounts of TFA (% v/v); (c) spectral changes of CHCl$_3$ solution of **2** in various acids (20% v/v); (d) absorption spectra of **1–3** in TFA/CHCl$_3$ solutions (8% v/v).
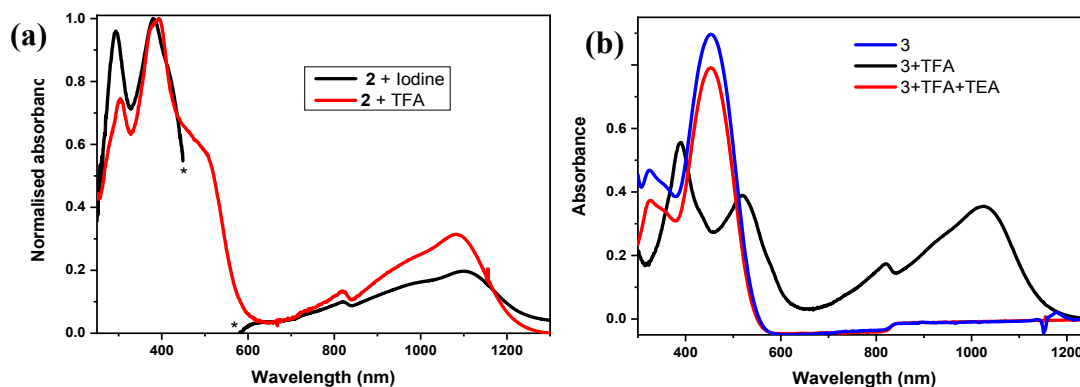
Fig. 3 a) UV-Vis absorption spectra of compound **2** in presence of TFA and Iodine in CHCl₃. ∗ Absorption due to Iodine was removed; b) UV-Vis absorption spectra of compound **3** after treating acid and neutralization (15 µM); After protonation and neutralization, 90% of the compound was isolated.

lack of such reversibility with Cs_2CO_3 suggests that Et_3N plays the role of a reducing agent restoring the original neutral compound (Fig. S9). The other acids such as trichloroacetic acids ($pK_a = 0.65$) which is only slightly weaker than TFA, Lewis acid ($BF_3 \cdot Et_2O$) and other strong Bronsted acids (hydrochloric, $pK_a = -6$; *p*-toluenesulfonic, $pK_a = -2.8$; methanesulfonic, $pK_a = -2.6$) tested, only a moderate ~100-150 nm red-shift of absorption took place (Fig. 2c). The control experiments with *tris*(4-aminophenyl)amine **7** also showed a large red-shift (from 300 to 680 nm) in TFA but only a minor shift of 30-80 nm in other tested acids (Fig. S15).

NMR and EPR studies:

To support the hypothesis of radical-cation formation, we recorded ¹H NMR and EPR spectra of **1-3** in presence of TFA. Upon addition of TFA, ¹H NMR signals of **3** display paramagnetic broadening, which is more pronounced for the enamine and triphenylamine moieties comparing to the 4-cyanophenyl group (Fig S14). The degassed solutions of **1-3** in the presence of TFA display a strong EPR signal with a *g*-value of ~2.003[57] (Fig. 4 and Fig. S18). The position and linewidth of this signal match well with iodine-oxidized **1-3**. It indeed

supports the hypothesis of radical cation formation in the presence of TFA. Protonation-induced formation of radical cations in strong electron donors has been previous reported for TTF and attributed to electron transfer from a neutral to protonated species.[58] Also a related acid-induced intramolecular electron transfer leading to open shell species have been recently observed for the quinoxaline-TTF.[53] The compound **7** was also found to be EPR active in TFA indicating that the formation of cation radical. However, no EPR signal has been observed for **1-3** and **7** in other acids (Fig. 4c and Fig. S18-19), indicating that the formation of cation radical is specific to TFA.
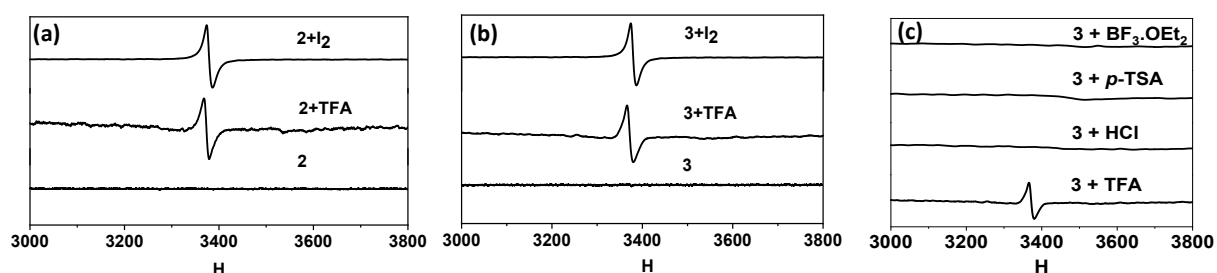

Fig. 4 EPR spectra of compounds **2** (a) and **3** (b) (10^{-3} M in toluene) in presence of excess of TFA (8% v/v) and I_2, (c) EPR spectra of compound **3** (10^{-3} M in toluene) in presence of different acids in excess.

Mechanism:

We speculate that the unique effect of TFA inducing formation of radical-cations upon protonation of **1-3**, could be attributed to electron transfer to TFA resulting in its irreversible decomposition thus shifting the unfavorable equillibrium (Scheme 2) towards radical-cation of the substrate ($S^{+\bullet}$). Indeed, the calculated barrier between the HOMO of **1** and LUMO of **1-H**$^+$ (1.1 eV, ~25 kcal/mol) is too high to allow for sufficient concentration of $1^{\bullet+}$ (Figure 5). Even for triply-protonated (**1-3H**)$^{3+}$ the electron transfer remains unfavorable by ~5 kcal/mol. On the other hand, redox-mediated decomposition of trifluoroacetate is well known,[59-62] and could provide the neccessary driving force for formation of the $1^{\bullet+}$. In this scenario, the electron

transfer from neutral (**S**) to protonated (**SH⁺**) ketoenamines **1-3** leads to formation of the observed radical cation **S⁺•** and neutral radical **S-H•**. The latter is a very strong donor (SOMO = -3.7 eV) (Fig. S25) and could be oxidized by TFA, recovering the neutral **S** which can again interact with **SH⁺** shifting the equilibrium to **S⁺•.** To prove that the radical-cation
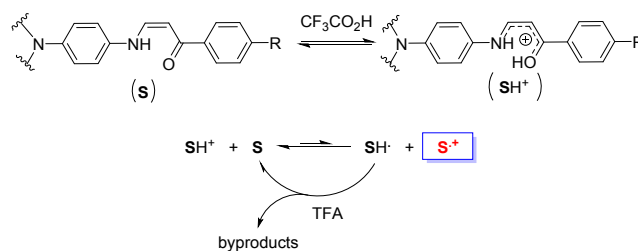
Scheme 2 Plausible mechanistic pathways of radical–cation formation in **1-3** (**S**) by interaction with TFA.
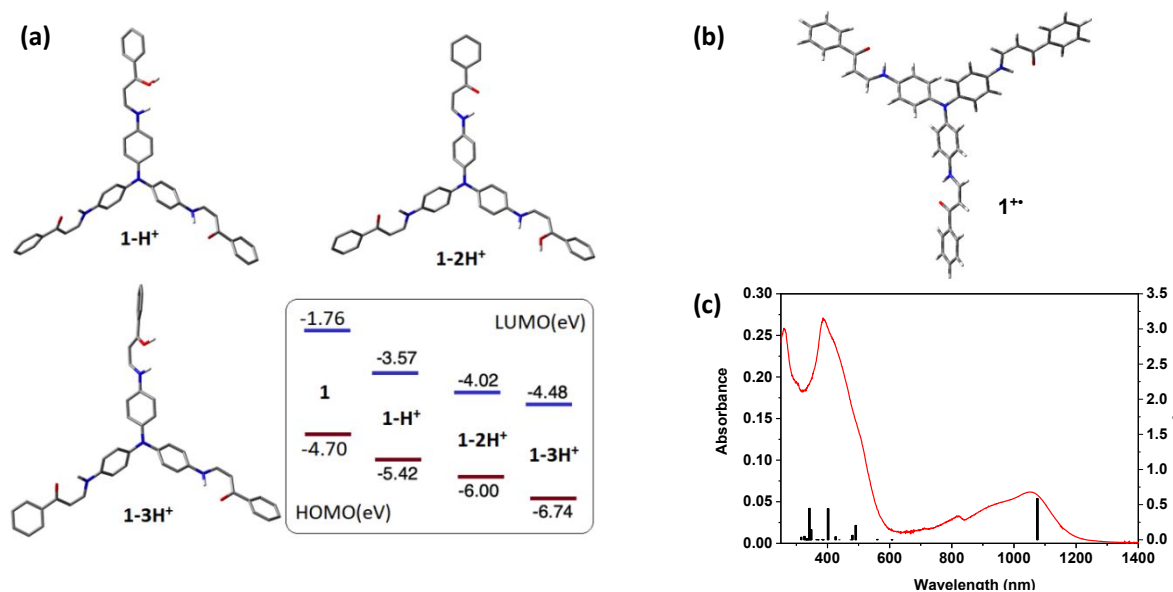
Fig. 5 (a) DFT-calculated (B3LYP/6-31G(d), CPCM solvent model) geometry optimized structures mono-, di-, and tri- protonated species of **1** and in the inset their HOMO and LUMO energies. (b) DFT geometry optimized structure of **1⁺•** (Using B3LYP level of theory, CPCM solvent model; chloroform) (c) overlay of experimental absorption spectrum of **1**+TFA and calculated TD-DFT spectrum of **1⁺•** (Using B3LYP level of theory, CPCM solvent model; chloroform).
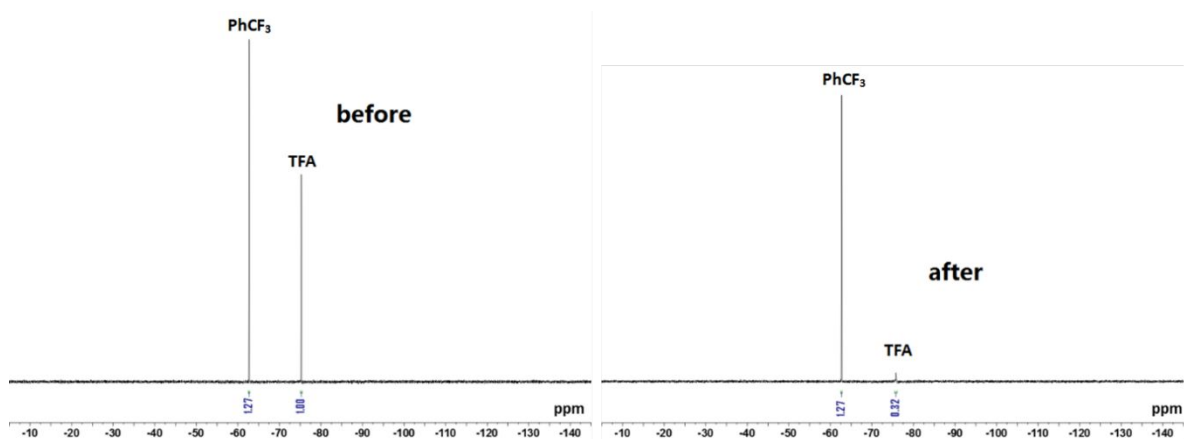
Fig. 6 ^{19}F NMR (400 MHz, CDCl$_3$) spectrum of TFA before and after the addition of 1 eq of TFA to **2**. PhCF$_3$ was added as an internal reference.

formation is driven by to the decomposition of TFA, we have performed ^{19}F NMR experiment before and after the addition of TFA to compound **2**. The experiment shows a ~70% decrease in TFA (with respect to the internal reference of PhCF$_3$) concentration after addition of **2** (Fig. 6). However, no fluorinated products were detected, presumably due to their high volatility. The loss of ^{19}F signal for TFA indeed supports that TFA undergoes a decomposition in the presence of **2**.

Conclusion

In summary, π-extended ketoenamine-substituted triarylamines **1-3** were synthesized *via* Michael addition-elimination reaction. These compounds exhibit intense absorption in the visible region (420-450 nm) resulting from intramolecular D-A interactions and weak fluorescence at ~500-720 nm. Upon exposure to strong Bronsted (stronger than CCl$_3$COOH) and Lewis acids, this absorption undergoes a moderate (100-150 nm) red-shift as a result of enhanced donor-acceptor interactions in the protonated species. Interestingly, treatment of **1-3** with TFA leads to a new NIR absorption band >1000 nm and strong EPR signal. This unexpected behaviour is attributed to single electron transfer from trifluoroacetate to the corresponding protonated triphenylamine, forming radical-cation species. The transformation is reversible and the initial compounds **1-3** can be recovered upon treatment with triethylamine.

We speculate that such redox instability of trilfluoroacetate can be employed in the *p*-doping of π-conjugated materials, despite its moderate Bronsted acidity.

Experimental Section

All chemicals were used as received unless otherwise noted. All solvents were of at least reagent grade and dried if necessary. Tris-(*p*-aminophenyl)amine[22] (TPA) were synthesized according to a previously published procedure. The ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on Bruker 400 or 500 MHz instruments. The frequency of 101 MHz is used for the ^{13}C nucleus. Tetramethylsilane was used as an internal standard for ^1H and ^{13}C NMR. Absorption and fluorescence spectra were obtained with Cary series UV-Vis-NIR spectrophotometer and Varian-Cary Eclipse spectrofluorometer, respectively. The fluorescence quantum yield (Φ_f) were estimated from emission and absorption spectra by the comparative method at the excitation wavelength of 390 nm using coumarin 153 ($\Phi_f = 0.9$ in toluene[59]) as the standard. Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were carried out with BAS electrochemical system utilizing the three-electrode configuration consisting of a glassy carbon as a working electrode, platinum wire as an auxiliary electrode and saturated calomel electrode as a reference. The experiments were done in dry CH_2Cl_2 using 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte. The instrument was calibrated using ferrocene as standard ($E_{Fc/Fc^+} = 0.3$ V). All the solutions were purged prior to electrochemical and spectral measurements with argon gas. The high-resolution mass spectra (HRMS) were recorded with a Bruker maxis Impact and Q-Tof micro mass spectrometer. For UV-vis and fluorescence titrations, the stock solution of all compounds (1×10^{-3} M) was prepared by using HPLC grade chloroform solvent. Electron spin resonance spectra were recorded with a Bruker EMX-plus X-band spectrometer ($\nu = 9.35$ GHz).

Keto-enol building blocks

A solution of acetophenone derivatives **8-10** (2.45 mmol) in 50 ml of THF was added dropwise to a solution of *t*-BuOK (1.37 g, 12.3 mmol) in 50 mL of THF) at -78 ºC for 1h under inert atmosphere. After stirring at the same temperature for additional 1 h, ethyl formate (1.81 g, 24.5 mmol) was added and allowed the reaction to warm up to room temperature and continued the stirring for 12 h. The reaction was quenched with 3 M HCl (30 mL) and the organic layer was extracted with ethyl acetate (3 × 100 mL) dried over $MgSO_4$ and concentrated in vacuo. The resultant solid was triturated with 50 mL of diethyl ether and filtered to obtain pure keto-enol derivatives.

Compound **4**: Yellow solid (260 mg, 73%). ^1H NMR was identical to the reported.[55]

Compound **5**: Yellow solid (300 mg, 73%). ^1H NMR (500 MHz, $CDCl_3$) δ 15.42 (s, 1H), 8.12 (d, J = 4.4 Hz, 1H), 7.88 (d, J= 9.0, 2H), 6.94 (d, J = 9.3 Hz, 2H), 6.15 (d, J = 4.5 Hz, 1H), 3.86 (s, 3H). **Note:** Compound found to be unstable in air. Thus, the crude compound was washed with hexanes to remove the unreacted starting material and directly taken to the next step.

Compound **6**: Yellow solid (325 mg, 74%). ^1H NMR (400 MHz, $CDCl_3$) δ 15.08 (s, 1H), 8.43 (d, J = 4.0 Hz, 1H), 7.99 (d, J = 8.5 Hz, 2H), 7.77 (d, J = 8.5 Hz, 2H), 6.24 (d, J = 4.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.60, 180.64, 138.59, 132.49, 127.76, 117.96, 115.95, 98.81.

Synthesis of TPA Derivatives

Keto-enol derivatives **4-6** (1.10 mmol), *tris*-(*p*-aminophenyl)amine **7** (100 mg, 0.34 mmol) and catalytic amounts of acetic acid (few drops) in ethanol (20 mL) were dissolved in ethanol and the mixture was heated to reflux at 80 ^0C for 12 h under nitrogen atmosphere. The resultant precipitate was filtered and washed with an excess of ethanol (50 mL) to obtain a pure product; orange solid.

Compound **1**: Orange solid (180 mg, 77%). ^1H NMR was identical to the reported.[55]

Compound **2**: Orange solid (210 mg, 79%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 12.15 (d, J = 12.3 Hz, 3H), 7.92 (d, J = 8.9 Hz, 6H), 7.42 (dd, J = 12.2, 7.9 Hz, 3H), 7.09 – 6.96 (m, 12H), 6.95 (d, J = 8.9 Hz, 6H), 5.97 (d, J = 7.9 Hz, 3H), 3.87 (s, 9H). ^{13}C NMR (101 MHz, CDCl3) δ 189.94, 162.61, 144.55, 143.64, 135.75, 132.19, 129.46, 125.24, 117.46, 113.83, 93.34, 55.59. HRMS (ESI-TOF): measured m/z = 771.3176; calculated m/z = 771.3177.

Compound **3**: Orange solid (200 mg, 76%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 12.33 (d, J = 12.5 Hz, 3H), 8.00 (d, J = 8.4 Hz, 6H), 7.75 (d, J = 8.4 Hz, 6H), 7.54 (dd, J = 12.5, 7.7 Hz, 3H), 7.15 – 6.94 (m, 12H), 5.98 (d, J = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 188.28, 146.13, 143.99, 142.78, 135.05, 132.32, 127.70, 125.16, 117.90, 114.66, 93.32. HRMS (ESI-TOF): measured m/z = 755.2630; calculated m/z= 755.2639.

Computational Details

All the calculations were performed using the Gaussian 09 program package. The density functional theory (DFT) method, hybrid functional uB3LYP with basis set 6-31G (d,p),[64,65] was used to optimize the geometries. The vertical excitation energies and oscillator strengths were obtained for the 50 lowest S0→Sn transitions at the optimized S0 state equilibrium geometries using the time-dependent density functional theory (TDDFT) method that was carried out at the same level of theory.[66-68] All the computations in the chloroform media were carried out using the self-consistent reaction field (SCRF) under the polarizable continuum model (CPCM).[66,67] The electronic absorption spectra, including wavelengths, were systematically investigated using TDDFT with the CPCM model based on the optimized ground structure.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgments

Keywords

References

1   J. Fabian, H. Nakazumi and M. Matsuoka, *Chem. Rev.*, 1992, **92**, 1197–1226.

2   L. Dou, Y. Liu, Z. Hong, G. Li and Y. Yang, *Chem. Rev.*, 2015, **115**, 12633–12665.

3   J. E. Anthony*, *Chem. Rev.*, 2006, **106**, 5028–5048.

4   A. Pron, P. Gawrys, M. Zagorska, D. Djurado and R. Demadrille, *Chem. Soc. Rev.*, 2010, **39**, 2577–2632.

5   K. Takimiya, S. Shinamura, I. Osaka and E. Miyazaki, *Adv. Mater.*, 2011, **23**, 4347–4370.

6   G. M. Fischer, M. Isomäki-Krondahl, I. Göttker-Schnetmann, E. Daltrozzo and A. Zumbusch, *Chem. – A Eur. J.*, 2009, **15**, 4857–4864.

7   L. C. Zhou, G. J. Zhao, J. F. Liu, K. L. Han, Y. K. Wu, X. J. Peng and M. T. Sun, *J.*

Photochem. Photobiol. A Chem., 2007, **187**, 305–310.

8   P.-A. Bouit, D. Rauh, S. Neugebauer, J. L. Delgado, E. Di Piazza, S. Rigaut, O. Maury, C. Andraud, V. Dyakonov and N. Martin, *Org. Lett.*, 2009, **11**, 4806–4809.

9   T. Geiger, H. Benmansour, B. Fan, R. Hany and F. Nüesch, *Macromol. Rapid Commun.*, 2008, **29**, 651–658.

10   Y. Wang, Z. Wang, J. Wang, Y. Wang, Z. Henderson, X. Wang, X. Zhang, J. Song and C. Lu, *Sci. Reports 2015 51*, 2015, **5**, 1–10.

11   K. Kawabata, M. Saito, I. Osaka and K. Takimiya, *J. Am. Chem. Soc.*, 2016, **138**, 7725–7732.

12   S. Ming, S. Zhen, K. Lin, L. Zhao, J. Xu and B. Lu, *ACS Appl. Mater. Interfaces*, 2015, **7**, 11089–11098.

13   C. An, M. Li, T. Marszalek, D. Li, R. Berger, W. Pisula and M. Baumgarten, *Chem. Mater.*, 2014, **26**, 5923–5929.

14   K. H. Hendriks, W. Li, M. M. Wienk and R. A. J. Janssen, *J. Am. Chem. Soc.*, 2014, **136**, 12130–12136.

15   L. Dou, C.-C. Chen, K. Yoshimura, K. Ohya, W.-H. Chang, J. Gao, Y. Liu, E. Richard and Y. Yang, *Macromolecules*, 2013, **46**, 3384–3390.

16   J. A. Love, I. Nagao, Y. Huang, M. Kuik, V. Gupta, C. J. Takacs, J. E. Coughlin, L. Qi, T. S. van der Poll, E. J. Kramer, A. J. Heeger, T.-Q. Nguyen and G. C. Bazan, *J. Am. Chem. Soc.*, 2014, **136**, 3597–3606.

17   J. D. Azoulay, Z. A. Koretz, B. M. Wong and G. C. Bazan, *Macromolecules*, 2013, **46**, 1337–1342.

18   H. Zhong, Z. Li, F. Deledalle, E. C. Fregoso, M. Shahid, Z. Fei, C. B. Nielsen, N. Yaacobi-Gross, S. Rossbauer, T. D. Anthopoulos, J. R. Durrant and M. Heeney, *J. Am. Chem. Soc.*, 2013, **135**, 2040–2043.

19   X. Guo, J. Quinn, Z. Chen, H. Usta, Y. Zheng, Y. Xia, J. W. Hennek, R. P. Ortiz, T. J. Marks and A. Facchetti, *J. Am. Chem. Soc.*, 2013, **135**, 1986–1996.

20   T. T. Steckler, P. Henriksson, S. Mollinger, A. Lundin, A. Salleo and M. R. Andersson, *J. Am. Chem. Soc.*, 2014, **136**, 1190–1193.

21   D. F. Perepichka and M. R. Bryce, *Angew. Chemie Int. Ed.*, 2005, **44**, 5370–5373.

22   G. Gattuso, G. Grasso, N. Marino, A. Notti, A. Pappalardo, S. Pappalardo and M. F. Parisi, *European J. Org. Chem.*, 2011, **2011**, 5696–5703.

23   O. Korostynska, K. Arshak, E. Gill and A. Arshak, *Sensors 2007, Vol. 7, Pages 3027-3042*, 2007, **7**, 3027–3042.

24   D. Aigner, S. M. Borisov, P. Petritsch and I. Klimant, *Chem. Commun.*, 2013, **49**, 2139–2141.

25   Y. Chen, C. Zhu, J. Cen, Y. Bai, W. He and Z. Guo, *Chem. Sci.*, 2015, **6**, 3187–3194.

26   Y. Yue, F. Huo, S. Lee, C. Yin and J. Yoon, *Analyst*, 2016, **142**, 30–41.

27   E. Kim, S. Lee and S. B. Park, *Chem. Commun.*, 2011, **47**, 7734–7736.

28   I. Steyaert, G. Vancoillie, R. Hoogenboom and K. De Clerck, *Polym. Chem.*, 2015, **6**, 2685–2694.

29   L. Van der Schueren and K. De Clerck, *Color. Technol.*, 2012, **128**, 82–90.

30   Y. Zhang, J. Garcia-Amorós, B. Captain and F. M. Raymo, *J. Mater. Chem. C*, 2016, **4**, 2744–2747.

31   P. S. Hariharan, E. M. Mothi, D. Moon and S. P. Anthony, *ACS Appl. Mater. Interfaces*, 2016, **8**, 33034–33042.

32   R. R. M, C.-W. Liao and S.-S. Sun, *J. Mater. Chem. C*, 2013, **1**, 6386–6394.

33   J. R. Swierk, N. S. McCool, T. P. Saunders, G. D. Barber and T. E. Mallouk, *J. Am. Chem. Soc.*, 2014, **136**, 10974–10982.

34   N. S. McCool, J. R. Swierk, C. T. Nemes, T. P. Saunders, C. A. Schmuttenmaer and T. E. Mallouk, *ACS Appl. Mater. Interfaces*, 2016, **8**, 16727–16735.

35   P. Zalar, Z. B. Henson, G. C. Welch, G. C. Bazan and T.-Q. Nguyen, *Angew. Chemie Int. Ed.*, 2012, **51**, 7495–7498.

36   G. C. Welch, R. Coffin, J. Peet and G. C. Bazan, *J. Am. Chem. Soc.*, 2009, **131**, 10802–10803.

37   H. V. Huynh, X. He and T. Baumgartner, *Chem. Commun.*, 2013, **49**, 4899–4901.

38   K. Cai, Q. Yan and D. Zhao, *Chem. Sci.*, 2012, **3**, 3175–3182.

39   J. A. Schneider and D. F. Perepichka, *J. Mater. Chem. C*, 2016, **4**, 7269–7276.

40   H. T. Black, I. Pelse, R. M. W. Wolfe and J. R. Reynolds, *Chem. Commun.*, 2016, **52**, 12877–12880.

41   T. Maeda and F. Würthner, *Chem. Commun.*, 2015, **51**, 7661–7664.

42   X. Ma, H. Niu, H. Wen, S. Wang, Y. Lian, X. Jiang, C. Wang, X. Bai and W. Wang, *J. Mater. Chem. C*, 2015, **3**, 3482–3493.

43   J. Weng, Q. Mei, W. Jiang, Q. Fan, B. Tong, Q. Ling and W. Huang, *Analyst*, 2013, **138**, 1689–1699.

44   P. Xue, P. Chen, J. Jia, Q. Xu, J. Sun, B. Yao, Z. Zhang and R. Lu, *Chem. Commun.*,

2014, **50**, 2569–2571.

45   M. O. Sandberg, O. Nagao, Z. Wu, M. M. Matsushita and T. Sugawara, *Chem. Commun.*, 2008, 3738–3740.

46   E. Cariati, C. Dragonetti, E. Lucenti, F. Nisic, S. Righetto, D. Roberto and E. Tordin, *Chem. Commun.*, 2014, **50**, 1608–1610.

47   L. Xu, H. Zhu, G. Long, J. Zhao, D. Li, R. Ganguly, Y. Li, Q.-H. Xu and Q. Zhang, *J. Mater. Chem. C*, 2015, **3**, 9191–9196.

48   T. Tang, T. Lin, F. Wang and C. He, *Phys. Chem. Chem. Phys.*, 2016, **18**, 18758–18766.

49   T. Tang, T. Lin, F. Wang and C. He, *J. Phys. Chem. B*, 2015, **119**, 8176–8183.

50   T. Tang, H. Chi, T. Lin, F. Wang and C. He, *Phys. Chem. Chem. Phys.*, 2014, **16**, 20221–20227.

51   W. Lu, J. Kuwabara and T. Kanbara, *Macromol. Rapid Commun.*, 2013, **34**, 1151–1156.

52   T. Tang, T. Lin, F. Wang and C. He, *Polym. Chem.*, 2014, **5**, 2980–2989.

53   J. S. Park, T. T. Tran, J. Kim and J. L. Sessler, *Chem. Commun.*, 2018, **54**, 4553–4556.

54   M.-J. Lin, B. Fimmel, K. Radacki and F. Würthner, *Angew. Chemie Int. Ed.*, 2011, **50**, 10847–10850.

55   M. R. Rao, Y. Fang, S. De Feyter and D. F. Perepichka, *J. Am. Chem. Soc.*, 2017, **139**, 2421–2427.

56   M. Ishikawa, M. Kawai and Y. Ohsawa, *Synth. Met.*, 1991, **40**, 231–238.

57   P. Data, P. Pander, P. Zassowski, V. Mimaite, K. Karon, M. Lapkowski, J. V.

Grazulevicius, P. Slepski and K. Darowicki, *Electrochim. Acta*, 2017, **230**, 10–21.

58   M. Giffard, P. Alonso, J. Garín, A. Gorgues, T. P. Nguyen, P. Richomme, A. Robert, J. Roncali and S. Uriel, *Adv. Mater.*, 1994, **6**, 298–300.

59   1   J. Fabian, H. Nakazumi and M. Matsuoka, *Chem. Rev.*, 1992, **92**, 1197–1226.

2   L. Dou, Y. Liu, Z. Hong, G. Li and Y. Yang, *Chem. Rev.*, 2015, **115**, 12633–12665.

3   J. E. Anthony*, *Chem. Rev.*, 2006, **106**, 5028–5048.

4   A. Pron, P. Gawrys, M. Zagorska, D. Djurado and R. Demadrille, *Chem. Soc. Rev.*, 2010, **39**, 2577–2632.

5   K. Takimiya, S. Shinamura, I. Osaka and E. Miyazaki, *Adv. Mater.*, 2011, **23**, 4347–4370.

6   G. M. Fischer, M. Isomäki-Krondahl, I. Göttker-Schnetmann, E. Daltrozzo and A. Zumbusch, *Chem. – A Eur. J.*, 2009, **15**, 4857–4864.

7   L. C. Zhou, G. J. Zhao, J. F. Liu, K. L. Han, Y. K. Wu, X. J. Peng and M. T. Sun, *J. Photochem. Photobiol. A Chem.*, 2007, **187**, 305–310.

8   P.-A. Bouit, D. Rauh, S. Neugebauer, J. L. Delgado, E. Di Piazza, S. Rigaut, O. Maury, C. Andraud, V. Dyakonov and N. Martin, *Org. Lett.*, 2009, **11**, 4806–4809.

9   T. Geiger, H. Benmansour, B. Fan, R. Hany and F. Nüesch, *Macromol. Rapid Commun.*, 2008, **29**, 651–658.

10   Y. Wang, Z. Wang, J. Wang, Y. Wang, Z. Henderson, X. Wang, X. Zhang, J. Song and C. Lu, *Sci. Reports 2015 51*, 2015, **5**, 1–10.

11   K. Kawabata, M. Saito, I. Osaka and K. Takimiya, *J. Am. Chem. Soc.*, 2016, **138**, 7725–7732.

12   S. Ming, S. Zhen, K. Lin, L. Zhao, J. Xu and B. Lu, *ACS Appl. Mater. Interfaces*, 2015, **7**, 11089–11098.

13   C. An, M. Li, T. Marszalek, D. Li, R. Berger, W. Pisula and M. Baumgarten, *Chem. Mater.*, 2014, **26**, 5923–5929.

14   K. H. Hendriks, W. Li, M. M. Wienk and R. A. J. Janssen, *J. Am. Chem. Soc.*, 2014, **136**, 12130–12136.

15   L. Dou, C.-C. Chen, K. Yoshimura, K. Ohya, W.-H. Chang, J. Gao, Y. Liu, E. Richard and Y. Yang, *Macromolecules*, 2013, **46**, 3384–3390.

16   J. A. Love, I. Nagao, Y. Huang, M. Kuik, V. Gupta, C. J. Takacs, J. E. Coughlin, L. Qi, T. S. van der Poll, E. J. Kramer, A. J. Heeger, T.-Q. Nguyen and G. C. Bazan, *J. Am. Chem. Soc.*, 2014, **136**, 3597–3606.

17   J. D. Azoulay, Z. A. Koretz, B. M. Wong and G. C. Bazan, *Macromolecules*, 2013, **46**, 1337–1342.

18   H. Zhong, Z. Li, F. Deledalle, E. C. Fregoso, M. Shahid, Z. Fei, C. B. Nielsen, N. Yaacobi-Gross, S. Rossbauer, T. D. Anthopoulos, J. R. Durrant and M. Heeney, *J. Am. Chem. Soc.*, 2013, **135**, 2040–2043.

19   X. Guo, J. Quinn, Z. Chen, H. Usta, Y. Zheng, Y. Xia, J. W. Hennek, R. P. Ortiz, T. J. Marks and A. Facchetti, *J. Am. Chem. Soc.*, 2013, **135**, 1986–1996.

20   T. T. Steckler, P. Henriksson, S. Mollinger, A. Lundin, A. Salleo and M. R. Andersson, *J. Am. Chem. Soc.*, 2014, **136**, 1190–1193.

21   D. F. Perepichka and M. R. Bryce, *Angew. Chemie Int. Ed.*, 2005, **44**, 5370–5373.

22   G. Gattuso, G. Grasso, N. Marino, A. Notti, A. Pappalardo, S. Pappalardo and M. F.

Parisi, *European J. Org. Chem.*, 2011, **2011**, 5696–5703.

23   O. Korostynska, K. Arshak, E. Gill and A. Arshak, *Sensors.,* 2007, **7**, 3027-3042.

24   D. Aigner, S. M. Borisov, P. Petritsch and I. Klimant, *Chem. Commun.*, 2013, **49**, 2139–2141.

25   Y. Chen, C. Zhu, J. Cen, Y. Bai, W. He and Z. Guo, *Chem. Sci.*, 2015, **6**, 3187–3194.

26   Y. Yue, F. Huo, S. Lee, C. Yin and J. Yoon, *Analyst*, 2016, **142**, 30–41.

27   E. Kim, S. Lee and S. B. Park, *Chem. Commun.*, 2011, **47**, 7734–7736.

28   I. Steyaert, G. Vancoillie, R. Hoogenboom and K. De Clerck, *Polym. Chem.*, 2015, **6**, 2685–2694.

29   L. Van der Schueren and K. De Clerck, *Color. Technol.*, 2012, **128**, 82–90.

30   Y. Zhang, J. Garcia-Amorós, B. Captain and F. M. Raymo, *J. Mater. Chem. C*, 2016, **4**, 2744–2747.

31   P. S. Hariharan, E. M. Mothi, D. Moon and S. P. Anthony, *ACS Appl. Mater. Interfaces*, 2016, **8**, 33034–33042.

32   R. R. M, C.-W. Liao and S.-S. Sun, *J. Mater. Chem. C*, 2013, **1**, 6386–6394.

33   J. R. Swierk, N. S. McCool, T. P. Saunders, G. D. Barber and T. E. Mallouk, *J. Am. Chem. Soc.*, 2014, **136**, 10974–10982.

34   N. S. McCool, J. R. Swierk, C. T. Nemes, T. P. Saunders, C. A. Schmuttenmaer and T. E. Mallouk, *ACS Appl. Mater. Interfaces*, 2016, **8**, 16727–16735.

35   P. Zalar, Z. B. Henson, G. C. Welch, G. C. Bazan and T.-Q. Nguyen, *Angew. Chemie Int. Ed.*, 2012, **51**, 7495–7498.

36   G. C. Welch, R. Coffin, J. Peet and G. C. Bazan, *J. Am. Chem. Soc.*, 2009, **131**, 10802–10803.

37   H. V. Huynh, X. He and T. Baumgartner, *Chem. Commun.*, 2013, **49**, 4899–4901.

38   K. Cai, Q. Yan and D. Zhao, *Chem. Sci.*, 2012, **3**, 3175–3182.

39   J. A. Schneider and D. F. Perepichka, *J. Mater. Chem. C*, 2016, **4**, 7269–7276.

40   H. T. Black, I. Pelse, R. M. W. Wolfe and J. R. Reynolds, *Chem. Commun.*, 2016, **52**, 12877–12880.

41   T. Maeda and F. Würthner, *Chem. Commun.*, 2015, **51**, 7661–7664.

42   X. Ma, H. Niu, H. Wen, S. Wang, Y. Lian, X. Jiang, C. Wang, X. Bai and W. Wang, *J. Mater. Chem. C*, 2015, **3**, 3482–3493.

43   J. Weng, Q. Mei, W. Jiang, Q. Fan, B. Tong, Q. Ling and W. Huang, *Analyst*, 2013, **138**, 1689–1699.

44   P. Xue, P. Chen, J. Jia, Q. Xu, J. Sun, B. Yao, Z. Zhang and R. Lu, *Chem. Commun.*, 2014, **50**, 2569–2571.

45   M. O. Sandberg, O. Nagao, Z. Wu, M. M. Matsushita and T. Sugawara, *Chem. Commun.*, 2008, 3738–3740.

46   E. Cariati, C. Dragonetti, E. Lucenti, F. Nisic, S. Righetto, D. Roberto and E. Tordin, *Chem. Commun.*, 2014, **50**, 1608–1610.

47   L. Xu, H. Zhu, G. Long, J. Zhao, D. Li, R. Ganguly, Y. Li, Q.-H. Xu and Q. Zhang, *J. Mater. Chem. C*, 2015, **3**, 9191–9196.

48   T. Tang, T. Lin, F. Wang and C. He, *Phys. Chem. Chem. Phys.*, 2016, **18**, 18758–18766.

49   T. Tang, T. Lin, F. Wang and C. He, *J. Phys. Chem. B*, 2015, **119**, 8176–8183.

50   T. Tang, H. Chi, T. Lin, F. Wang and C. He, *Phys. Chem. Chem. Phys.*, 2014, **16**, 20221–20227.

51   W. Lu, J. Kuwabara and T. Kanbara, *Macromol. Rapid Commun.*, 2013, **34**, 1151–1156.

52   T. Tang, T. Lin, F. Wang and C. He, *Polym. Chem.*, 2014, **5**, 2980–2989.

53   J. S. Park, T. T. Tran, J. Kim and J. L. Sessler, *Chem. Commun.*, 2018, **54**, 4553–4556.

54   M.-J. Lin, B. Fimmel, K. Radacki and F. Würthner, *Angew. Chemie Int. Ed.*, 2011, **50**, 10847–10850.

55   M. R. Rao, Y. Fang, S. De Feyter and D. F. Perepichka, *J. Am. Chem. Soc.*, 2017, **139**, 2421–2427.

56   Y. Zhu, W. Weng, T. Zhou, Z. Lin, N. Ding, P. Maitarad, C. Wang and J. Guo, *Chem. Commun.*, 2022, **58**, 6606–6609.

57   P. Data, P. Pander, P. Zassowski, V. Mimaite, K. Karon, M. Lapkowski, J. V. Grazulevicius, P. Slepski and K. Darowicki, *Electrochim. Acta*, 2017, **230**, 10–21.

58   M. Giffard, P. Alonso, J. Garín, A. Gorgues, T. P. Nguyen, P. Richomme, A. Robert, J. Roncali and S. Uriel, *Adv. Mater.*, 1994, **6**, 298–300.

59   A. Studer, *Angew. Chemie Int. Ed.*, 2012, **51**, 8950–8958.

60   C. Lai and T. E. Mallouk, *J. Chem. Soc. Chem. Commun.*, 1993, 1359–1361.

61   M. Chen and S. L. Buchwald, *Angew. Chemie Int. Ed.*, 2013, **52**, 11628–11631.

62   MatsuiKiyohide, TobitaEtsuko, AndoMidori and KondoKiyosi, *Chem. Lett.*, 2006, **10**, 1719–1720.

63   A. M. Brouwer, *Pure Appl. Chem.*, 2011, **83**, 2213–2228.

64   W. J. Hehre, *Acc. Chem. Res.*, 1976, **9**, 399–406.

65   O. Treutler and R. Ahlrichs, *J. Chem. Phys.*, 1995, **102**, 346–354.

66   M. Cossi, N. Rega, G. Scalmani and V. Barone, *J. Comput. Chem.*, 2003, **24**, 669–681.

67   V. Barone and M. Cossi, *J. Phys. Chem. A*, 1998, **102**, 1995–2001.

68   R. Bauernschmitt and R. Ahlrichs, *Chem. Phys. Lett.*, 1996, **256**, 454–464.