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Journal Name

COMMUNICATION

Dimesitylboryl Functionalised Cyanostilbene Derivatives of Phenothiazine: Distinctive Polymorphism Dependent Emission and Mechanofluorochromism†

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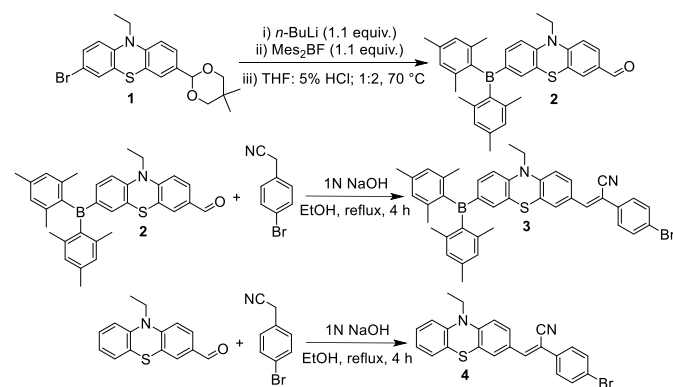
Organic π -conjugated compounds showing polymorphic and mechanofluorochromic (MFC) behaviors are promising candidates for many potential applications in materials chemistry. Herein, we report two distinct molecular designs based on phenothiazine as donor and triarylborane and cyanostilbene as acceptors. For example, Acceptor-Donor-Acceptor system (A-D-A; compound 3) and Donor-Acceptor (D-A; compound 4) moieties, in which 3 exhibits polymorphism with two distinct emissions (yellow and red). The single crystal X-ray diffraction analyses of 3 clearly show two conformational isomers. The color of the emission can be altered by grinding or fuming process.

Organic π -conjugated luminescent materials have received increasing attention in recent years due to their potential for applications in organic light emitting diodes (OLED), mechanochromic materials, sensors and switches, bioimaging and so on.¹ However, conventional fluorophores suffer from reduced or completely quenched fluorescence in the aggregated/solid state due to strong intermolecular π - π stacking, which activates non-radiative decay channels.² This detrimental phenomenon is known as aggregation quenching or aggregation-caused quenching (ACQ)³ that limits the practical applicability of many conventional fluorophores.⁴ However, the aggregation-induced emission (AIE), a phenomenon that operates just opposite to ACQ overcomes the difficulties associated with the latter.^{5,6} In this respect, Tang and co-workers have established that the restriction of the intramolecular rotation (RIR) and/or restriction of intramolecular vibration (RIV) of the aromatic rings in the solid or aggregated state is responsible for enhanced emission. These two processes are collectively termed as restriction of intramolecular motions (RIM).⁷ On the other hand, conjugation-induced rigidity (CIR) effect in twisted molecular

systems fills the gap between ACQ and AIE luminogens, thus providing dual-state emissive materials (emitting in solution and solid state) suitable for promising applications.⁸

During crystallization process rotations within the molecules are prevented, resulting in conformational polymorphs with different emissions in the solid state.⁹ Gu and co-workers have demonstrated that the emission for di(*p*-methoxyphenyl)dibenzofulvene is dependent on the polymorphic form in the solid state.¹⁰ For example, one polymorph exhibits yellow-green fluorescence and the other displays strong blue-emission. Interestingly, amorphous solid exhibits weak orange fluorescence. Utilizing supramolecular co-crystallization, Yan and co-workers showed that organic crystals could be easily tuned to give different emissions from blue to green.¹¹ 2,7-Diphenylfluorenone derivatives, reported by Yuan and co-workers, displayed reversible, stimuli-responsive, solid-state emission switching by altering the mode of crystal packing.¹²

Recently, phenothiazine-based molecules have received a great deal of attention due to their non-planar butterfly-like structure, which regulates π - π stacking, and as a result reduces non-radiative decay channels leading to enhanced emission in the aggregated/solid state.¹³ Based on the structural information available in the Cambridge Structural Database (CSD), there are many phenothiazine-based molecules known that show interesting optical properties with diverse structural



Scheme 1 Synthetic routes for compounds 3 and 4

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Table 1 Optical properties of **2-4** in THF

Compound	λ_{abs} (nm)	λ_{em} (nm)	Φ^a	S.S
2	293, 319 (sh), 412	531	0.51	5439
3	320, 443	589	0.27	5595
4	316, 419	590	0.17	6917

^aQuantum yields were referenced against fluorescein (0.1 M NaOH, $\lambda_{\text{ex}} = 350$ nm, $\Phi = 0.89$) and using the following equation $\Phi = \Phi_{\text{r}} \times I/I_{\text{r}} \times A_{\text{r}}/A \times (\eta/I_{\text{r}})^2$. Where Φ = quantum yield, I = integrated emission intensity, A = absorbance, η = refractive index of solvent, R = reference.

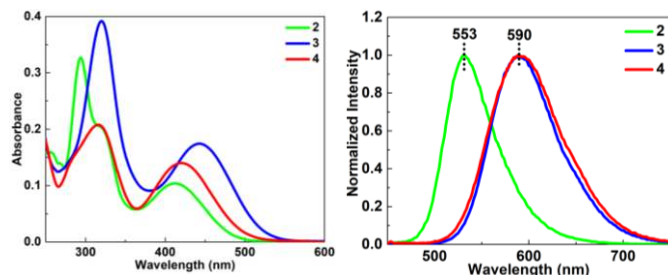


Fig. 1 UV-Vis spectra of **2-4** in THF (10^{-5} M) (left) and fluorescence spectra of **2-4** in THF (10^{-5} M) (right) (excitation wavelengths are at their longer λ_{max} observed in UV-Vis spectra).

features.¹⁴ Triaryboranes are known for their electron accepting features and provide sufficient steric hindrance to control the molecular stacking.¹⁵ On the other hand, cyanostilbene is another class of compound with cyano-substituted stilbenic π -conjugated backbone that offers excellent optoelectronic properties.¹⁶ As these moieties are known for their crystalline type of assembly, we hypothesize that these systems might generate a sterically encumbered acceptor-donor-acceptor system with multiple-state emissive properties.

The key precursor **2** was synthesized by protecting 7-bromo-10-ethyl-10H-phenothiazine-3-carbaldehyde with neopentylglycol and by successive reaction with *n*-BuLi, Mes_2BF , followed by subsequent hydrolysis with 10% HCl in THF (See ESI for details). Compound **3** was prepared by a simple Knoevenagel condensation reaction of 4-bromophenylacetonitrile with the triarylborane-phenothiazine aldehyde (Scheme 1). We presume that the charge transfer features of compound **3** will be better than that of **2**, and hence would enhance emission in the solid state. Compound **4** was prepared as a control.

Compounds **2-4** are soluble in common organic solvents but are insoluble in water and fully characterized by multinuclear NMR (^1H , ^{13}C , ^{11}B) spectroscopy and HRMS analysis. The compounds **2-4** are stable in air and moisture. In addition, thermogravimetric analysis (TGA) for **2-4** showed that decomposition started at around 300 °C under N_2 at 5% weight loss (Fig. S20, ESI). Also, the molecular structure of compounds **3-4** was unambiguously determined by single crystal X-ray diffraction analysis (Fig. S25-32).

THF solutions (10 μM) of compounds **2-4** displayed two major absorption bands in the range of 280-450 nm (Table 1 and Fig. 1 left). The higher energy bands (<320 nm) can be attributed to the combined aryl-centred π - π^* and boryl based

π - π (B) transitions. The lower energy band of **3** (443 nm) showed a bathochromic shift in comparison to those of **2** (412 nm) and **4** (419 nm). This is due to the combined effect of delocalization/conjugation through the vacant p orbital of tricoordinate boron as well as the presence cyano-stilbene unit of **3**. These assignments are comparable with those of related compounds reported for other dimesitylboryl phenothiazine and cyano-stilbene compounds.¹⁷ In emission studies, THF solutions of **2** showed a peak at 553 nm, **3** and **4** showed peaks at 590 nm when excited at their longest absorption maxima (Fig. 1 right). Furthermore, the emission properties of compounds **2-4** were explored in different solvents of varying polarities (Table S1). Unlike absorption properties, the emission properties of these compounds are notable and displayed significant solvatochromism with higher Stokes shifts (Table 1). The solvatochromic shift for compound **4** is higher than those of **2** and **3**, which may be due to the presence of sterically bulky $-\text{BMe}_2$ substituents in **2** and **3**. Compounds **2** and **3** showed higher emission quantum yields (Φ) in solvents of different polarities in comparison to those of **4**. Fluorescence lifetimes were recorded in cyclohexane and the decay traces were double exponential in nature (Table S3, ESI). The nonradiative decay rate constant (k_{nr}) for **4** ($2.5 \times 10^8 \text{ s}^{-1}$) was higher than those of **2** ($0.6 \times 10^8 \text{ s}^{-1}$) and **3** ($1.4 \times 10^8 \text{ s}^{-1}$), which indicates that compound **4** loses a major fraction of its excited state energy through nonradiative decay pathways.

DFT and TD-DFT calculations were carried out to gain a better understanding of the optical properties of the compounds, with B3LYP hybrid functional and 6-31G (d) basis set. The optimized geometries of **2-4** were in good agreement with the single crystal X-ray structures (Fig. S5-7). In all the compounds HOMO is mainly located on phenothiazine moiety while the LUMO in compound **2** is delocalized over dimesitylboryl and aldehyde units. In contrast to **2**, the LUMOs in **3** and **4** are mainly located on a cyano-stilbene fragment of the molecules (Fig. 2 and S8). Furthermore, the calculated HOMO-LUMO gaps in **2-4** are agreeing well with those observed experimentally.

Compounds **2-4** exhibited high photoluminescence in their solid state, with the emission peaks at 517, 606 and 623, respectively (Fig. 3, S11, and S18). The trend observed in the solid-state emission is similar to that observed in a solution state. In the case of compound **4**, red-shifted emission was observed due to the high planar nature of the compound, as

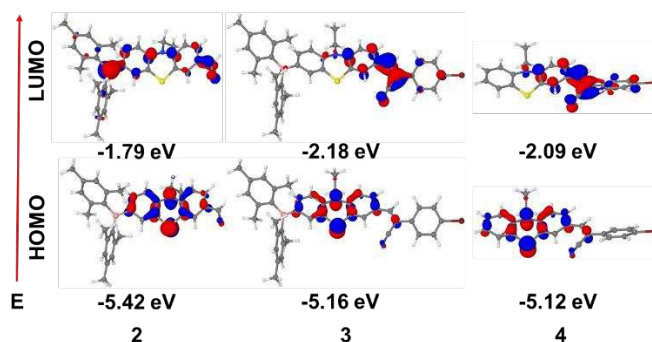


Fig. 2 Frontier molecular orbital diagrams of **2-4** with energies.

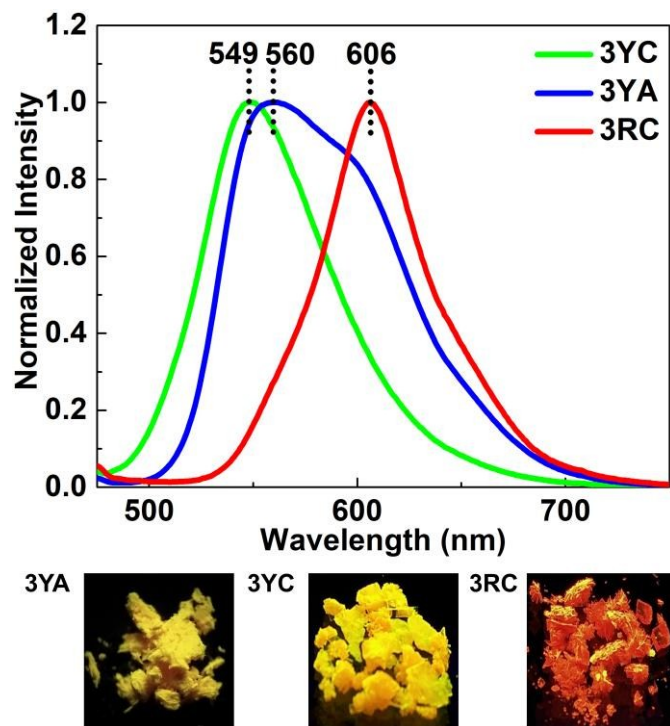


Fig. 3 Emission spectra of polymorphs **3YA**, **3YC** and **3RC** in solid state (top) and their corresponding photographs taken under UV light ($\lambda = 365$ nm) irradiation (bottom).

evidenced by the single crystal X-ray diffraction (SXRD) analysis.

To gain more insight into the molecular packing of the compounds **3-4**, they were crystallized in “solvent or different solvents”. Compound **3** crystallized in two forms, viz., yellow (**3YC**) and red (**3RC**). Besides that, we have also isolated yellow amorphous form (**3YA**) [detailed syntheses of three forms of **3** are provided in ESI]. The solid-state X-ray structures of polymorphs **3** and compound **4** are shown in Fig. 4. Both polymorphic crystals **3YC** and **3RC** forms have highly twisted structure, originating from the steric congestion between the mesityl groups on the boron atom and the puckered nature of phenothiazine molecules. The presence of dimesitylboron moiety helps to crystallize the compound in two forms. Due to the puckered nature of **3YC**, the effective pseudo conjugation

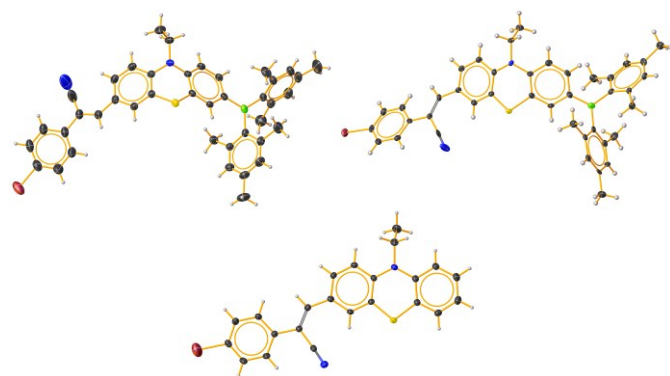


Fig. 4 Molecular structure of **3YC** (top left), **3RC** (top right) and **4** (bottom) with ellipsoids probability of 50%. Disordered hydrogen atoms on the methyl groups have been removed for clarity. Color codes: black = carbon; grey = hydrogen; blue = nitrogen; green = boron; yellow = sulfur; brown = bromine.

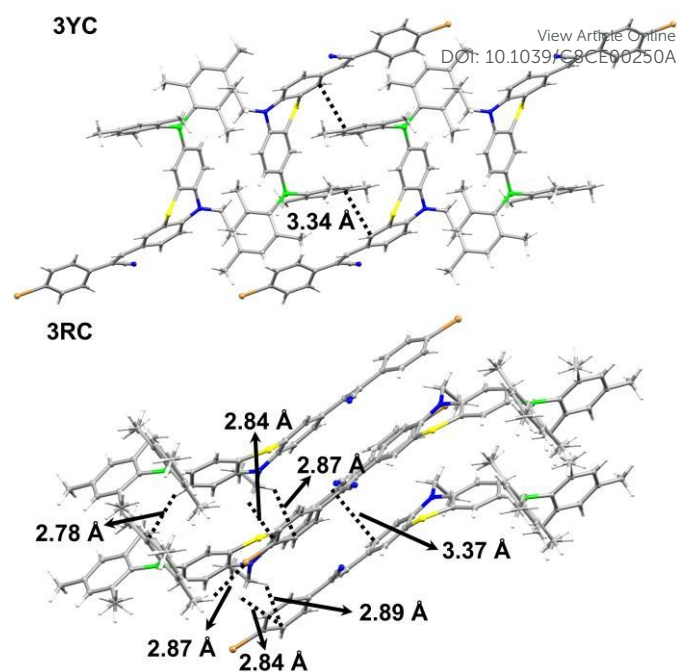


Fig. 5 Crystal packing modes as well as short contacts of **3YC** and **3RC**.

is disturbed compared to that present in **3RC**, thus giving yellow (549 nm) and red (606 nm) fluorescence in the solid state, respectively.

The boron atom in compound **3** (**3YC** and **3RC**) has a trigonal-planar configuration with the sum angles around boron atom being 360° . The B–C(aryl) bond length in **3RC** (1.557 Å) is shorter than that observed in **3YC** (1.583 Å) and longer than that of 4-(dimesitylboryl)-N,N-dimethylaniline (1.545(2) Å).¹⁸ In contrast, the B–C(mes) bond lengths follow the opposite trend. Both crystals **3RC** and **3YC** lack the possibility of π - π stacking in their solid state. **3RC** exhibited somewhat planar structure when compared to a **3YC** structure in the solid state and thus the emission of **3RC** is red shifted. In both crystal forms of compound **3** (**3YC** and **3RC**) exhibits intermolecular CH \cdots π interactions, such interactions help lock the motion of the aryl rings to rigidify the molecular conformation (Fig. 5, S26 and S28 and Tables S5 and S6).¹⁹ Now the excitons can undergo radiative relaxation, resulting in enhanced emission in the solid state.²⁰ Compound **4** crystallized in monoclinic space group (P 2₁/n) (Fig. S31). The crystal structure of **4** exhibited a folding angle of phenothiazine being 171.34° with a tilt angle of 8.66° , which is a near planar geometry. According to Dhamodharan *et al.* there are only six phenothiazine based neutral compounds known to show near planar geometry stabilized by intra as well as the intermolecular interaction between the molecules.²¹ The compound **4** adds one more entry into the library of phenothiazine based neutral planar molecular systems.¹⁴

The fluorescence response of compounds **2-4** to various stimuli such as mechanical and solvent fuming (vapor digestion) was investigated, in which **2** exhibited a good response to mechanical stimulus. As shown in Fig. 6, under UV light the color of compound **2** changed from green (517 nm) to



Fig. 6 Color changes of compound **2** upon grinding and fuming process under UV light irradiation at 365 nm.

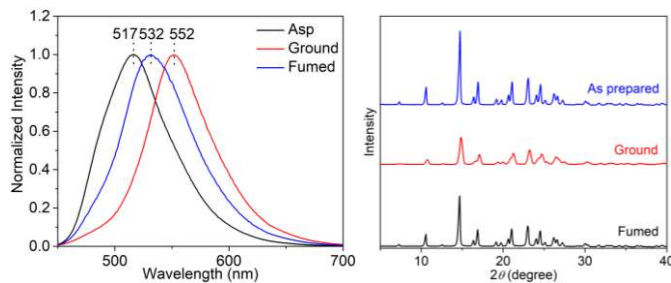


Fig. 7 Normalized PL spectra of **2** under different conditions (left) and Powder XRD diffractions of **2** under different conditions (right).

yellow fluorescence (552 nm) upon grinding. The mechanofluorochromic (MFC) property of **2** has also been supported by powder X-Ray diffraction (PXRD) studies (Fig. 7). This phenomenon is typical mechanofluorochromism and suppression of PXRD peaks may be attributed to amorphousization of compound **2**. Fuming with dichloromethane (DCM) vapors partially reverted the sample back to its crystalline form (Fig. 7 right).

Upon grinding, polymorphs **3YC** and **3YA** exhibit a change in the fluorescence from yellow to red, which may be due to planarization of the molecules from the twisted structure. In the case of **3RC**, grinding and fuming process induces a marginal change in their fluorescence spectra (Fig. S13). This marginal change in fluorescence spectra of **3RC** may be attributed to the near planar structure observed in crystals of **3RC** compared to the structure of **3YC**. The PXRD analyses were carried out to understand the mechanofluorochromic behavior of the fluorophores. The compounds **3YC** and **3RC** show different crystalline peaks in PXRD whereas **3YA** exhibited a broad PXRD pattern indicating its amorphous nature (Fig. S14, right). Upon grinding, **3YA** exhibited little change in its PXRD pattern and solvent exposure did not change the pattern much and looks similar to that of **3RC**. In **3YC**, grinding and fuming led to a greater change in PXRD patterns, which may be due to planarization of the molecules and change of crystallinity. Such type of crystal-to-crystal phase transitions due to mechano-response have been well established in inorganic systems by H. Ito *et al.*²² Upon grinding, **3RC** led to considerable change in its PXRD pattern and upon fuming the peaks were partially regained. Many of the gold complexes exhibit polymorphic changes during the exposure to solvent vapors.²³ Even though BMe₂ group gives enough steric congestion in the case of polymorphs of **3**, grinding process mostly results in planarization of the molecules. To know the stability of the polymorphs **3YA**, **3YC** and **3RC**, differential scanning calorimetry (DSC) analysis was carried out. The enthalpies of phase transitions (melting) of the three compounds are -39.44 J/g, -71.86 J/g and -66.23 J/g, respectively (Fig. S21-24). From the DSC analyses, it is

apparent that both the crystalline forms of **3** (**3YC** and **3RC**) are more stable than that of amorphous one (**3YA**). Compound **4** failed to exhibit any mechanofluorochromism as evidenced from its fluorescence spectra and PXRD analysis (Fig. S18); this may be due to highly planar nature of the compound as observed from the SXRD analysis. Note that compound **4** was used as a control in order to verify whether the absence of BMe₂ unit generates any structural changes in the crystalline forms.

In summary, synthesis, characterization and photophysical properties of triarylborane-phenothiazine-cyanostilbene derivatives have been described. The A-D-A and D-A types of compounds are synthesized using dimesitylboron and cyanostilbene as acceptors and phenothiazine as a donor. The dimesitylboron derivative (**3**) shows two crystalline forms (**3YC** and **3RC**) and one amorphous form (**3YA**). All the compounds **2-4** exhibit bright fluorescence in the solid state. Compounds **2**, **3YA**, **3YC** and **3RC** show significant mechanofluorochromic behavior. Owing to their stimuli-responsive luminescence, these triarylborane based polymorphs reported in this article may find potential applications in smart materials and optoelectronics.

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Conflicts of Interest

There are no conflicts to declare.

Notes and references

- 1 a) Organic Light-Emitting Materials and Devices (Eds.: Z. Li, H. Meng), CRC Press, Boca Raton, 2006; b) I. D. W. Samuel, G. A. Turnbull, *Chem. Rev.* 2007, **107**, 1272-1295; c) S. W. Thomass III, G. D. Joly, T. M. Swager, *Chem. Rev.* 2007, **107**, 1339-1386; d) Z. Chi, X. Zhang, B. Xu, X. Zhou, C. Ma, Y. Zhang, S. Liu, J. Xu, *Chem. Soc. Rev.* 2012, **41**, 3878-3896; e) B. Daly, J. Ling, A. P. Silva, *Chem. Soc. Rev.* 2015, **44**, 4203-4211; f) T. D. Ashton, K. A. Jolliffe, F. M. Pfeffer, *Chem. Soc. Rev.* 2015, **44**, 4547-4595
- 2 T. M. Figueira-Duarte, K. Mullen, *Chem. Rev.* 2011, **111**, 7260-7314.
- 3 J. B. Birks, *Photophysics of Aromatic Molecules*, Wiley, London, 1970.
- 4 C. W. Tang, S. A. Vanslyke, *Appl. Phys. Lett.* 1987, **51**, 913-915.
- 5 J. Luo, Z. Xie, J. W. Y. Lam, L. Cheng, H. Chen, C. Qiu, H. S. Kwok, X. Zhan, Y. Liu, D. Zhu, B. Z. Tang, *Chem. Commun.* 2001, **0**, 1740-1741.

- 6 J. Mei, N. L. C. Leung, R. T. K. Kwok, J. W. Y. Lam, B. Z. Tang, *Chem. Rev.* 2015, **115**, 11718-11940.
- 7 a) J. Mei, Y. Hong, J. W. Y. Lam, A. Qin, Y. Tang, B. Z. Tang, *Adv. Mater.* 2014, **26**, 5429-5479; b) Z. Zhao, B. He, B. Z. Tang, *Chem. Sci.* 2015, **6**, 5347-5365.
- 8 G. Chen, W. Li, T. Zhou, Q. Peng, D. Zhai, H. Li, W. Z. Yuan, Y. Zhang, B. Z. Tang, *Adv. Mater.* 2015, **27**, 4496-4501.
- 9 X. Wang, Z.-Z. Li, S.-F. Li, H. Li, J. Chen, Y. Wu, H. Fu, *Adv. Optical Mater.* 2017, 1700027.
- 10 X. Gu, J. Yao, G. Zhang, Y. Yan, C. Zhang, Q. Peng, Q. Liao, Y. Wu, Z. Xu, Y. Zhao, H. Fu, D. Zhang, *Adv. Funct. Mater.* 2012, **22**, 4862-4872.
- 11 D. Yan, A. Delori, G. Lloyd, T. Friščić, G. Day, W. Jones, J. Lu, M. Wei, D. Evans, X. Duan, *Angew. Chem. Int. Ed.* 2011, **50**, 12483-12486.
- 12 M. Yuan, D. Wang, P. Xue, W. Wang, J. Wang, Q. Tu, Z. Liu, Y. Liu, Y. Zhang, J. Wang, *Chem. Mater.* 2014, **26**, 2467-2477.
- 13 a) X. Zhu, R. Liu, Y. Li, H. Huang, Q. Wang, D. Wang, X. Zhu, S. Liu, H. Zhu, *Chem. Commun.* 2014, **50**, 12951-12954; b) Z. Xie, C. Chen, S. Xu, J. Li, Y. Zhang, S. Liu, J. Xu, Z. Chi, *Angew. Chem. Int. Ed.* 2015, **54**, 7181-7184; c) G. Zhang, J. Sun, P. Xue, Z. Zhang, P. Gong, J. Peng, R. Lu, *J. Mater. Chem. C* 2015, **3**, 2925-2932.
- 14 CSD searched and archived cif file is attached as an ESI.
- 15 a) F. Jäkle, *Chem. Rev.* 2010, **110**, 3985-4022; b) L. Ji, S. Griesbeck, T. B. Marder, *Chem. Sci.* 2017, **8**, 846-863; c) S. K. Sarkar, S. Mukherjee, P. Thilagar, *Inorg. Chem.* 2014, **53**, 2343-2345; d) Z. M. Hudson, S. Wang, *Acc. Chem. Res.* 2009, **42**, 1584-1596; e) C. R. Wade, A. E. J. Broomsgrove, S. Aldridge, F. P. Gabbaï, *Chem. Rev.* 2010, **110**, 3958-3984; f) A. Wakamiya, K. Mori, S. Yamaguchi, *Angew. Chem. Int. Ed.* 2007, **46**, 4273-4276; g) E. Januszewski, A. Lorbach, R. Grewal, M. Bolte, J. W. Bats, H.-W. Lerner, M. Wagner, *Chem. Eur. J.* 2011, **17**, 12696-12705; h) G. R. Kumar, P. Thilagar, *Dalton Trans.* 2014, **43**, 7200-7207; i) Y. Ren, F. Jäkle, *Dalton Trans.* 2016, **45**, 13996-14007.
- 16 a) B.-Y. An, J. Gierschner, S. Y. Park, *Acc. Chem. Res.*, 2012, **45**, 544-554; b) M. Martínez-Abadía, R. Giménez, M. B. Ros, *Adv. Mater.*, 2017, 1704161; c) E. Ravindran, N. Somanathan, *J. Mater. Chem. C*, 2017, **5**, 4763-4774.
- 17 a) C. Arivazhagan, A. Maity, K. Bakthavachalam, A. Jana, S. K. Panigrahi, E. Suresh, A. Das, S. Ghosh, *Chem. Eur. J.* 2017, **23**, 7046-7051; b) Y.-J. Cheng, S.-Y. Yu, S.-C. Lin, J. T. Lin, L.-Y. Chen, D.-S. Hsiu, Y. S. Wen, M. M. Lee, S.-S. Sun, *J. Mater. Chem. C* 2016, **4**, 9499-9508; c) J. H. Park, K. C. Ko, E. Kim, N. Park, J. H. Ko, D. H. Ryu, T. K. Ahn, J. Y. Lee, S. U. Son, *Org. Lett.* 2012, **14**, 5502-5505; d) E. Ravindran, N. Somanathan, *J. Mater. Chem. C*, 2017, **5**, 7436-7440.
- 18 Z. Yuan, C. D. Entwistle, J. C. Collings, D. Albesa-Jové, A. S. Batsanov, J. A. K. Howard, N. J. Taylor, H. M. Kaiser, D. E. Kaufmann, S. Poon, W. Y. Wong, C. Jardin, S. Fathallah, A. Boucekkine, J.-F. Halet, T. B. Marder, *Chem. Eur. J.* 2006, **12**, 2758-2771.
- 19 a) M. J. Percino, M. Cerón, P. Ceballos, G. Soriano-Moro, O. Rodríguez, V. M. Chapela, M. E. Castro, J. Bonilla-Cruz, M. A. Siegler, *CrystEngComm.* 2016, **18**, 7554-7572; b) H. Zhang, Z. Zhang, K. Ye, J. Zhang, Y. Wang, *Adv. Mater.*, 2006, **18**, 2369-2372; c) L. Currie, J. Fernandez-Cestau, L. Rocchigiani, B. Bertrand, S. J. Lancaster, D. L. Hughes, H. Duckworth, S. T. E. Jones, D. Credgington, T. J. Penfold, M. Bochmann, *Chem. Eur. J.* 2017, **23**, 105-113.
- 20 W. Z. Yuan, X. Y. Shen, H. Zhao, J. W. Y. Lam, L. Tang, P. Lu, C. Wang, Y. Liu, Z. Wang, Q. Zheng, J. Z. Sun, Y. Ma, B. Z. Tang, *J. Phy. Chem. C* 2014, **114**, 6090-6099.
- 21 E. Ramachandran, R. Dhamodharan, *J. Mater. Chem. C* 2015, **3**, 8642-8648.
- 22 a) M. Jin, T. S. Chung, T. Seki, H. Ito, M. A. Garcia-Garibay, *J. Am. Chem. Soc.* 2017, **139**, 18115-18121; b) M. Jin, T. Seki, H. Ito, *J. Am. Chem. Soc.* 2017, **139**, 7452-7455.
- 23 a) M. A. Malwitz, S. H. Lim, R. L. White-Morris, D. M. Pham, M. M. Olmstead, A. L. Balch, *J. Am. Chem. Soc.* 2012, **134**, 10885-10893; b) S. H. Lim, M. M. Olmstead, A. L. Balch, *Chem. Sci.* 2013, **4**, 311-318; c) S. H. Lim, M. M. Olmstead, A. L. Balch, *J. Am. Chem. Soc.* 2011, **133**, 10229-10238.

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SYNOPSIS TOC

Dimesitylboryl Functionalised Cyanostilbene Derivatives of Phenothiazine: Distinctive Polymorphism Dependent Emission and MechanofluorochromismC. Arivazhagan, Partha Malakar, R. Jagan, Edamana Prasad* and Sundargopal Ghosh^{a, *}

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Dimesitylborane functionalized cyanostilbene derivatives of phenothiazine exhibit polymorphism with distinct solid-state emissions.

