# **RSC Advances**



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This Accepted Manuscript will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/advances

# Journal Name

# **RSCPublishing**

## ARTICLE

Cite this: DOI: 10.1039/xoxx00000x

Received ooth January 2012, Accepted ooth January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

# AIE-active mechanochromic materials based Nphenylcarbazol-substituted tetraarylethene for OLED applications

He Zhao, <sup>a</sup> Yang Wang, <sup>b</sup> Yongtao Wang, <sup>a</sup>\* Gufeng He, <sup>b</sup>\* Mei Xue, <sup>a</sup> Pingan Guo, <sup>a</sup> Bin Dai, <sup>a</sup>\* Zhiyong Liu<sup>a</sup> and Yu Qi <sup>a</sup>

Multifunctional optoelectronic materials are important in both theoretical and practical application aspects. In this study, three luminogen-based N-phenylcarbazol-substituted tetraarylethene, namely NPCE, MeNPCE and MeONPCE, were designed and synthesised via Friedel–Crafts acylation and McMurry coupling reaction. All of the luminogens show typical aggregation-induced emission (AIE) characteristics with high solid-state efficiency of up to 83%. The dyes also exhibit excellent thermal stability ( $T_d$  of up to 434 °C) and prominent morphological stability. In addition, only MeONPCE reveals obvious mechanochromism (emission wavelength change of up to 64 nm). This proved introduce methoxy group in one of the phenyl rings at para position can easily obtain mechanochromic materials. The organic light-emitting diodes (OLEDs) that use these dyes as nondoped emission layer emit cyan light with current efficiency and external quantum efficiency of 7.87 cd A<sup>-1</sup> and 3.87%, respectively. In comparison, the mutilayer organic light-emitting diodes adopting MeONPCE as nondoped emission layer revealing that MeONPCE is an eximious p-type light emitter.

### Introduction

Organic fluorescent dyes have drawn considerable attention because of their unique photochemical properties. Efficient organic fluorescent materials have been designed and synthesised for application in various fields, such as chemosensors and organic light-emitting diodes (OLEDs).1-7 However, most traditional dyes suffered from the thorny aggregation-caused quenching (ACQ) problem due to molecular aggregation. Therefore, most practical applications of organic fluorescent materials were restricted, especially for optoelectronics and biophotonics.<sup>8-11</sup> Fortunately, Tang's group discovered an intriguing aggregation-induced emission (AIE) phenomenon compared with ACQ effect; AIE dyes are more efficiently emit in the aggregated state than in the dissolved form. The AIE phenomenon is caused by the restriction of intramolecular rotations (RIR) in the aggregated solid, which offers the possibility to obtain high solid-state efficiency and an active area of research for their potential applications.<sup>12-14</sup>

Recently, a great deal of attention is being paid to the AIEactive mechanochromic materials and electroluminescence materials. On the one hand, solid emitters that show changes in fluorescence colour upon mechanical stimuli can be applied in memory chips, sensors, camouflaging security inks and other optoelectronic devices because of their fundamental importance and potential applications.<sup>7, 15-19</sup> AIE molecules with propellerlike twisted conformation can bring about loose molecular packings, which are easily destroyed under external mechanical stimuli, resulting in changes of fluorescence colour.<sup>16</sup> Hence, AIE-active compounds have been considered as a well of mechanochromic materials. On the other hand, AIE molecules exhibit high solid fluorescence quantum efficiency owing to restrictinintramolecular motion, which is helpful to enhance the maximum external quantum efficiency ( $EQE_{max}$ ) of light emitting layer in OLEDs. Normally, AIE-active luminogens, even nondoped OLEDs, exhibit great performance owing to their high solid-state efficiencies.<sup>20-22</sup>

Although AIE-active mechanochromic or electroluminescence luminogens are no longer novel materials after years of wide investigation, multifunctional optoelectronic materials with AIE-active, mechanochromic and electroluminescence are rarely found. То achieve а multifunctional optoelectronic material, herein, one Nphenylcarbazol-substituted tetraarylethene luminogens, namely MeONPCE (Chart 1), was designed and synthesised. Carbazole MeONPCE will facilitate on possessing units in electroluminescence and hole-transporting properties.<sup>23, 24</sup> More importantly, methoxy groups can influence packing pattern of MeONPCE on the solid state, thereby easily obtaining mechanochromic materials by conversion of morphology or polymorphs, and enhancing solid state emission by restricting rotation of intramolecular<sup>25, 26</sup>. For comparison, NPCE and MeNPCE were also designed and synthesised (Chart 1).

Journal Name



Chart 1 Chemical structures and photophysical properties of NPCE, MeNPCE and MeONPCE;  $\lambda_{aps}$  and  $\lambda_{gs}$  stand for the maximum emission wavelength of as prepared solid and ground solid,  $\Phi_{F,s}$  and  $\Phi_{F,aps}$  stand for the quantum efficiencies of the dye molecules in dilute solution and in as prepared solid,  $\alpha_{AIE}$  stand for the corresponding AIE factors.

Three compounds exhibit typical AIE-active, excellent thermal stability and high solid-state photoluminescence quantum yields (PLQY) of up to 83%. The organic light-emitting diodes utilizing these dyes as light emitter and hole transporter simultaneously emit cyan light with current efficiency and *EQE* of 7.87 cd  $A^{-1}$  and 3.87%, respectively. As was expected, MeONPCE also shows distinct mechanochromism (emission wavelength change of up to 64 nm), the hole-transporting properties as well as 4,4'-bis [N-(1-naphthyl)-N-phenyl-amino] biphenyl (NPB).

### **Results and discussion**

### Synthesis

The molecular structures of the three new AIE luminogens were designed. Scheme S1 shows the synthetic route of the carbazole-containing AIE luminogens NPCE, MeNPCE and MeONPCE. Firstly, the Friedel-Crafts acylation of benzoyl chloride derivatives and 9-phenyl-carbazole synthesised 1a-1c (Scheme 1),<sup>27</sup> which were then converted into three target compounds by a Zn/TiCl<sub>4</sub>-catalysed McMurry coupling reaction afterwards.28, 29 All of the intermediates and final products were carefully purified and fully characterized by NMR and mass spectroscopy, from which satisfactory data corresponding to the expected molecular structures were obtained. Details of the synthetic procedures and characterization data were presented in the ESI. McMurry coupling of NPCE, MeNPCE and MeONPCE resulted in two different isomers with a ratio of about 1:1 calculated from the <sup>1</sup>H NMR spectra. All of the luminogens are soluble in common organic solvents, such as tetrahydrofuran, chloroform toluene and dichloromethane, but are insoluble in water.

### **Optical properties**

When the target compounds were dissolved in pure THF solvent, no visible light was observed under UV light, whereas their aggregated powders emitted bright yellow-green light and blue light. The emission spectra of the luminogens were further determined in THF and THF/water mixtures. Water was used

because it is a typical poor solvent for the target compounds in which they are aggregated. The target compounds are almost non-fluorescent in pure THF solutions (10 µM). As depicted in Fig. 1A, at water fractions  $(f_w) \leq 60\%$ , the fluorescence intensity of MeONPCE shows extremely weak signals, which is attributed to the dissolved luminogens with active intramolecular rotations. When the water fraction is increased to 70%, the emission intensity of MeONPCE increases because the solvating power of the mixture is worsened, thereby leading to molecular aggregation. The molecular aggregation can result in planarized conformations, which generate increased effective conjugation lengths, thus producing much redder emissions.<sup>30</sup> (Fig.1A). Moreover, the mixture polarity has also a little impact on spectral shift for D- $\pi$ -D conjugated molecules. At a f<sub>w</sub> of 90%, the emission is significantly strengthened by <144-fold compared with that in pure THF (Fig. 1B). Moreover, the contrast images given in the inset of Fig. 1B shows that its AIE nature. Similar phenomena are also observed in NPCE and MeNPCE, with an emission enhancement of >111- and 102fold with 90% water content compared with those in THF (Fig. S9 and S10). Clearly, the emission of luminogens is induced by aggregate formation. In a dilute solution, the rotation of multiple phenyl rings effectively consumes exciton energies and the nonluminescent molecules in solutions. In the aggregated state, the restriction of RIR allows the dye molecules to emit intensely. However, aqueous mixtures have no precipitate in the macroscopic view, indicating that the aggregates are nanodimensional. To prove this point, transmission electron microscope (TEM) images were obtained (Fig. S11) and the absorption of the luminogens in THF and THF/water mixtures were tested. As shown in Fig. S12, their absorption spectra show obvious level-off tails at the longwavelength region with high water content, which is due to the scattering effect of the luminogen nanoparticles.<sup>31, 32</sup>



Fig. 1 (A) Emission spectra of MeONPCE in THF and THF/water mixtures with varying water fractions (f<sub>w</sub>). (B) Emission intensity increase of MeONPCE in different aqueous mixtures. Concentration: 10  $\mu$ M; excitation wavelength: 360 nm. The photographs in (B) are MeONPCE in THF and 10/90 THF-water mixture taken under 365 nm UV light illumination.

To evaluate the emissions quantitatively, the quantum efficiencies of the dye molecules in dilute solution ( $\Phi_{F,s}$ ) and in as-prepared solid ( $\Phi_{F,aps}$ ) states were further investigated. The  $\Phi_{F,s}$  values of NPCE, MeNPCE and MeONPCE are as low as 0.1%, 0.1% and 0.1%, respectively, which were estimated in THF using quinine sulfate ( $\Phi_{F,s} = 54\%$  in 0.1 N H<sub>2</sub>SO<sub>4</sub>) as

standard. However, the  $\Phi_{F,aps}$  of NPCE, MeNPCE and MeONPCE, which were measured using a calibrated integrating sphere, are as high as 82%, 66% and 83%, respectively, with the corresponding AIE factors ( $\alpha_{AIE} = \Phi_{F,aps}/\Phi_{F,s}$ ) of 820, 660 and 830 (Chart 1). These results further validate their AIE activity. In addition, MeNPCE shows a lower efficiency of 66% than NPCE and MeONPCE, which might be attributed to the vibration and rotation of the methyl group, thereby leading to exciton energy consumption even in the solid state.<sup>8</sup>

### Mechanochromic

The AIE characteristic and high solid-state efficiency render the dyes promising mechanochromic materials.<sup>16</sup> Therefore, their solid emission properties were examined by grinding the as-prepared solids of luminogens. Interestingly, aside from the high quantum efficiencies of the solid states, another remarkable difference was that the luminogens MeONPCE showed mechanochromic fluorescent behaviour. As shown in Fig. 2, the as-prepared solid powder of MeONPCE emits a skyblue light at 441 nm wavelength. When the as-prepared solid powder was ground with a mortar, the sky-blue powder turned into cyan-emissive solids with a maximum at 505 nm. Normally, luminogens with mechanochromic character can be easily restored by annealing or fuming treatment. However, when MeONPCE was heated at 60, 80, 100 and 120 °C for more than 5 h (even overnight), the cyan emission colours cannot be restored. The result proves its stable conformations due to the high glass-transition temperature ( $T_g = 134.2$  °C) of ground powders (Fig. 3A). Such steady conformation and emission are beneficial for optoelectronic applications.<sup>33</sup> Nevertheless, upon further fuming with dichloromethane or ethyl acetate vapour for 3 min, the original blue emission is recovered. The reversibility of mechanochromic conversion was checked by the grinding-vapour exposure processes. As depicted in Fig. S13, switching between blue and green emission colours can be repeated with many cycles without fatigue because of the non-destructive nature of the mechanical stimuli. These surveys further demonstrate the remarkable morphological stability of amorphous solids. The mechanochromic fluorescent behaviour of luminogens normally transforms from crystals to amorphous solids,<sup>34-36</sup> and amorphous solids are always applied in OLEDs. Thus, the research suggests that MeONPCE has potential applications for EL material because of its excellent thermal stability and efficient solid-state emission.

To obtain information on the mechanism, powder X-ray diffraction (XRD) analysis was conducted. The as-prepared powder exhibits much intense and sharp diffraction peak in Fig. 2B, which is indicative of their regular crystalline structure. No diffraction peak is observed with mechanical grinding, which reflects a disordered molecular packing. When fumed with solvent, sharp diffractions emerge again, which indicated the restoration of an ordered crystalline lattice. The results further prove that mechanochromism was extremely associated with the arrangement of molecules, which highly influence the photophysical properties.<sup>37</sup> However, similar phenomena are not observed in NPCE and MeNPCE. Mechanochromic usually depends on the mode of these molecular packing.<sup>16</sup> This further proved introduce methoxy group in one of the phenyl rings at para position can easily obtain mechanochromic materials.



Fig. 2 (A) Emission spectra of the as-prepared, ground and fumed MeONPCE solids, (B) their XRD patterns and (C and D) their photographs taken under UV illumination.

### Thermal and electrochemical properties

In terms of device fabrication and operation, high thermal and morphological stability is vitally important. Thus, the thermal properties of the luminogens were evaluated. Thermal gravimetric analysis (TGA) (Fig. 3 and S14) results indicated that all luminogens are thermally stability, with  $T_d$  (defined as the temperature at which a sample loses its 5% weight) values from 278 °C to 434 °C. The curves obtained by differential scanning calorimetry (DSC) (Fig. 3A), which was used to study the behaviour of as prepared MeONPCE under heating, showed two glass-transition temperatures ( $T_{g1} = 35.9$  °C and  $T_{g2} = 93.9$  °C) caused by the coexistence of cis- and trans-isomers of the MeONPCE molecule. The  $T_g$  value of NPCE and MeNPCE are as high as 106.6 and 138.6 °C, respectively. These performances are sufficient for their potential applications in OLED preparation.



Fig. 3 (A) DSC of the as prepared and ground MeONPCE solids. (B) TGA thermograms of MeONPCE recorded under nitrogen atmosphere at 10  $^\circ C$  min–1 scan rates.

Carbazole derivatives are known to possess high energy levels of highest occupied molecular orbital (HOMO) and excellent charge transport properties.<sup>38</sup> Thus, the

Journal Name

electrochemical properties of luminogens were investigated by cyclic voltammetry at 50 mV·s<sup>-1</sup> scan rate. As shown in Fig. 4, MeONPCE displayed reversible oxidation process in dry DCM solution. The oxidation peak was found at 0.80 V. Therefore, HOMO energy was obtained from the onset oxidation potential corresponding to -5.2 eV. The E<sub>g</sub> value of 3.34 eV was obtained from solution absorption spectra according to published method.<sup>39, 40</sup> The LUMO of MeONPCE was -1.86 eV, obtained by subtracting its E<sub>g</sub> value from its HOMO value. Similar results were obtained in NPCE and MeNPCE (Fig. S15). The band gap energies, HOMO and LUMO levels of NPCE, MeNPCE and MeONPCE are summarized in Table S1. The electrochemical properties that characterize the dye molecules can be applied in electroluminescent devices.<sup>41</sup>



Fig. 4 Representative cyclic voltammogram of MeONPCE measured in dry dichloromethane solution with 0.1 M TBAPF $_6$  at 25 °C.

### **Electroluminescence properties**

The high photoluminescence (PL) efficiency and good thermal stability of luminogens encouraged us to evaluate their electroluminescence (EL) properties. Three simple OLEDs were fabricated with non-doped dyes as emissive layer. NPB doped with 6% 2,3,5,6-tetrafluoro-7,7,8,8tetracyanoquinodimethane (F4-TCNQ) was used as holeinjection layer (HIL), and 1,3,5-tris(N-phenylbenzimidazole-2yl)benzene (TPBI) was used as electron-transporting layer, followed by 1 nm LiF as electron injection layer. Hence, the basic device structure is ITO/NPB:F4-TCNQ (20 nm, 6%)/X (30 nm)/TPBI (40 nm)/LiF (1 nm)/Al, where X is NPCE (device I), MeNPCE (device II) or MeONPCE (device III). All devices emit cyan light with maximum EL ( $\lambda_{EL}$ ) of 498, 487 and 492 nm, respectively, which are similar to the PL emissions of amorphous solids (502, 498 and 499 nm). The results reveal that the EL originated from the amorphous film (Fig. S16). Moreover, the device with MeNPCE as emissive layer (EML) exhibits a maximum EQE of 3.87%, which is quite high for non-doped EML OLED (Table 1). All three devices have turnon voltages below 3.5 V, which strongly prove that NPCE, MeNPCE and MeONPCE possess good hole-transporting property. The three AIE materials possess a slightly higher HOMO level than NPB (5.4 eV); hence, the hole-injection barrier between HIL and EML can be neglected. Therefore, the order of the hole-transporting capability can be roughly

estimated from their current density–voltage (J-V) characteristics (Fig. 5A): MeONPCE > MeNPCE > NPCE. This order agrees well with the donor power of the three compounds.



For comparison, a device with 10 nm NPB instead of 10 nm dye layer in device III was constructed and its configuration is ITO/NPB:F4-TCNQ (20 nm, 6%)/NPB (10nm)/ MeONPCE (20 nm) /TPBI (40 nm)/LiF (1 nm)/Al (device IV). Devices IV and III had almost identical J-V characteristics (Fig. 5A), which was a strong hint that MeONPCE has similar holetransporting ability to NPB. Significantly, the CIE coordinates were almost kept unchanged from (0.23, 0.37) to (0.23, 0.39) in Fig. S17. These results implied the inherent hole-transporting capability of carbazole-containing luminogens. Fig. 5B shows that all devices have better luminance when the current were set to compliance. Fig. 6 describes the current efficiency (CE) and EQE vs. voltage characteristics of the four devices. All EL data are summarized in Table 1. Although these devices are not yet further optimized, the results clearly prove that carbazolecontaining AIE luminogens as solid light emitters or holetransporting materials are promising for the construction of advanced OLEDs.





| ournal Name | ourn | al N | ame |
|-------------|------|------|-----|
|-------------|------|------|-----|

|  | fable 1. EL | performances | of NPCE. | MeNPCE | and MeONPCE.4 |
|--|-------------|--------------|----------|--------|---------------|
|--|-------------|--------------|----------|--------|---------------|

| Device | $\lambda_{max}$ (nm) | V <sub>on</sub><br>(v) | $\begin{array}{c} CE_{ma} \\ (cd A^{-1}) \end{array}$ | EQE<br>(%) |
|--------|----------------------|------------------------|---|------------|
| Ι      | 498                  | 4.4                    | 6.45  | 2.77       |
| Π      | 485                  | 4.4                    | 7.87  | 3.87       |
| III    | 490                  | 3.2                    | 6.44  | 2.90       |
| IV     | 494                  | 3.2                    | 6.82  | 2.75       |

<sup>*a*</sup> Device structures: without HTL, ITO/NPB:F4-TCNQ (20 nm,6%)/X (30 nm)/TPBI (40 nm)/LiF (1 nm)/AI; X = NPCE (I), MeNPCE (II), MeONPCE (III); with HTL, ITO/NPB:F4-TCNQ (20 nm, 6%)/NPB(10 nm)/ MeONPCE (20 nm)/TPBI (40 nm)/LiF (1 nm)/AI (IV). Abbreviations:  $\lambda_{EL} = EL$  maximum,  $V_{on}$  = turn-on voltage at 1 cd m<sup>-2</sup>, CE<sub>max</sub> = maximum current efficiency, *EQE*<sub>max</sub> = maximum external quantum efficiency.

### Conclusions

The rational design of luminescent molecules is of importance to achieve efficient multifunctional optoelectronic materials with AIE-active, mechanochromic and electroluminescence. In this study, three dyes based on N-phenylcarbazol-substituted tetraarylethene, namely NPCE, MeNPCE and MeONPCE were designed and synthesized. The impacts of substituent groups in tetraarylethene AIE-active, mechanochromic on and were electroluminescence properties of the luminogens investigated in detail. With the increase of the electrondonating ability of the substituents, it was found that the holetransporting properties were enhanced in OLEDs. Three luminogens all show typical AIE characteristics with high solid-state efficiency of up to 83%, excellent thermal stability ( $T_d$  up to 434 °C) and high morphological stabilities. Among them, only MeONPCE exhibits remarkable mechanochromism conversion  $(\Delta \lambda \Box up)$ to 64 nm). Moreover, the mechanochromism can be repeatedly switched many times without fatigue by simple grinding-fuming processes, which indicated the introduction of hydrophilic groups in hydrophobic tetraarylethene can easily change molecule packing pattern on the solid state, and obtain mechanochromic materials. The OLEDs that were fabricated using the luminogens as both holetransporting and light-emitting layer materials shown high CEmax and EQE of up to 7.87 cd  $A^{-1}$  and 3.87%, respectively. To compare MeONPCE with traditional hole-transporting material, a device with HTL was constructed, and the results indicate that the hole-transporting ability of NPB and MeONPCE are almost the same. The results show that carbazole-containing AIE luminogens are promising solid light emitters or hole-transporting materials for the construction of advanced OLEDs.

### Acknowledgements

This work was financially supported by the Key Programs for Science and Technology Development of Shihezi University (Rczx201017, GXJS2013-ZDGG02) and the Postgraduate Technology Innovation Program of Xinjiang (XJGRI2014052).

### Notes and references

<sup>*a*</sup> School of Chemistry and Chemical Engineering/Key Laboratory for Green Processing of Chemical Engineering of Xinjiang Bingtuan, Shihezi University, Shihezi 832003, Xinjiang, P. R. China.

E-mail: wyt\_shzu@163.com; dbinly@126.com; Fax: +86993 2057270; Tel: +86 993 2057277

<sup>b</sup> National Engineering Lab for TFT-LCD Materials and Technologies, and Department of Electronic Engineering, Shanghai Jiao Tong University, Shanghai 200240, P. R.China. E-mail: gufenghe@situ.edu.cn.

† Electronic Supplementary Information (ESI) available: [Experimental section, characterization data, absorption and emission spectra, and other materials of synthetic procedures.]. See DOI:10.1039/b000000x/

### References

- A. Mishra, C. Uhrich, E. Reinold, M. Pfeiffer and P. Bäuerle, Adv Energy Mater, 2011, 1, 265-273.
- R. Fitzner, E. Mena-Osteritz, A. Mishra, G. Schulz, E. Reinold, M. Weil, C. Körner, H. Ziehlke, C. Elschner and K. Leo, *J Am Chem Soc*, 2012, 134, 11064-11067.
- P. L. Wu, X. J. Feng, H. L. Tam, M. S. Wong and K. W. Cheah, *J Am Chem Soc*, 2008, 131, 886-887.
- B. K. An, J. Gierschner and S. Y. Park, Accounts Chem Res, 2011, 45, 544-554.
- Y. H. Jiang, Y. C. Wang, J. L. Hua, J. Tang, B. Li, S. X. Qian and H. Tian, *Chem Commun*, 2010, 46, 4689-4691.
- W. Z. Yuan, Y. Y. Gong, S. Chen, X. Y. Shen, J. W. Y. Lam, P. Lu, Y. Lu, Z. Wang, R. Hu, N. Xie, H. S. Kwok, Y. Zhang, J. Z. Sun and B. Z. Tang, *Chem Mater*, 2012, 24, 1518-1528.
- Y. Y. Gong, Y. Zhang, W. Z. Yuan, J. Z. Sun and M. Y. Zhang, J Phys Chem C, 2014, 118, 10998-11005.
- Y. Y. Gong, Y. Tan, J. Liu, P. Lu, C. Feng, W. Z. Yuan, Y. Lu, J. Z. Sun, G. He and M. Y. Zhang, *Chem Commun*, 2013, 49, 4009-4011.
- S. Kim, Q. Zheng, G. S. He, D. J. Bharali, H. E. Pudavar, A. Baev and P. N. Prasad, *Adv Funct Mater*, 2006, 16, 2317-2323.
- Z. R. Grabowski, K. Rotkiewicz and W. Rettig, *Chem Rev*, 2003, 103, 3899-4032.
- S. W. Thomas, G. D. Joly and T. M. Swager, *Chem Rev*, 2007, 107, 1339-1386.
- J. D. Luo, Z. L. Xie, J. W. Y. Lam, L. Cheng, H. Y. Chen, C. F. Qiu, H. S. Kwok, X. W. Zhan, Y. Q. Liu and D. B. Zhu and B. Z. Tang, *Chem Commun*, 2001, 21, 1740-1741.
- C. Y. K. Chan, J. W. Y. Lam, Z. Zhao, S. Chen, P. Lu, H. H. Y. Sung, H. S. Kwok, Y. Ma, I. D. Williams and B. Z. Tang, *J Mater Chem C*, 2014, 2, 4320-4327.
- W. Z. Yuan, P. Lu, S. Chen, J. W. Lam, Z. Wang, Y. Liu, H. S. Kwok, Y. Ma and B. Z. Tang, *Adv Mater*, 2010, 22, 2159-2163.
- 15. Y. Sagara and T. Kato, Nat Chem, 2009, 1, 605-610.
- Z. Chi, X. Zhang, B. Xu, X. Zhou, C. Ma, Y. Zhang, S. Liu and J. Xu, *Chem Soc Rev*, 2012, 41, 3878-3896.
- W. Z. Yuan, Y. Tan, Y. Y. Gong, P. Lu, J. W. Y. Lam, X. Y. Shen, C. Feng, H. H. Y. Sung, Y. Lu, I. D. Williams, J. Z. Sun, M. Y. Zhang and B. Z. Tang, *Adv Mater*, 2013, 25, 2837-2843.
- X. Luo, J. Li, C. Li, L. Heng, Y. Q. Dong, Z. Liu, Z. Bo and B. Z. Tang, *Adv Mater*, 2011, 23, 3261-3265.
- B. Xu, M. Xie, J. He, B. Xu, Z. Chi, W. Tian, L. Jiang, F. Zhao, S. Liu, Y. Zhang, Z. Xu and J. Xu, *Chem Commun*, 2013, 49, 273-275.

- 20. H. S. Kwok and B. Z. Tang, Chem Commun, 2013, 49, 594-596.
- 21. Z. Guo, W. Zhu and H. Tian, Chem Commun, 2012, 48, 6073-6084.
- X. P. Wang, Y. Qian, T. J. Zhu, M. M. Cai, B. X. Mi, X. Y. Jiang, Z. Q. Gao, W. Huang and Z. L. Zhang, *Phys Status Solidi A*, 2012, 209, 373-377.
- 23. X. Huang, S. Zhong, X. Yan, X. Ke, N. Srisanit and M. R. Wang, *Synthetic Met*, 2004, 140, 79-86.
- 24. C. S. Oh, C. W. Lee and J. Y. Lee, *Dyes Pigments*, 2013, 98, 372-376.
- 25. D. Frath, J. Massue, G. Ulrich and R. Ziessel, *Angewandte Chemie*, 2014, 53, 2290-2310.
- P. Galer, R. C. Korosec, M. Vidmar and B. Sket, J Am Chem Soc, 2014, 136, 7383-7394.
- 27. Y. Feng, Q. R. Chen, W. S. Li and C. Xie, *Chem Res Appl*, 2007, 19, 1162-1165.
- R. Hu, J. L. Maldonado, M. Rodriguez, C. Deng, C. K. W. Jim, J. W. Y. Lam, M. M. F. Yuen, G. Ramos-Ortiz and B. Z. Tang, *J Mater Chem*, 2012, 22, 232-240.
- X. F. Duan, J. Zeng, Z. B. Zhang and G. F. Zi, *J Org Chem*, 2007, 72, 10283-10286.
- M. Grell, D. Bradley, G. Ungar, J. Hill and K. Whitehead, Macromolecules, 1999, 32, 5810-5817.
- Z. Zhao, S. Chen, J. W. Y. Lam, P. Lu, Y. Zhong, K. S. Wong, H. S. Kwok and B. Z. Tang, *Chem Commun*, 2010, 46, 2221-2223.
- Y. Liu, X. Ye, G. Liu, Y. Lv, X. Zhang, S. Chen, J. W. Y. Lam, H. S. Kwok, X. Tao and B. Z. Tang, *J Mater Chem C*, 2014, 2, 1004-1009.
- Y. Y. Gong, J. Liu, Y. Zhang, G. He, Y. Lu, W. B. Fan, W. Z. Yuan, J. Z. Sun and M. Y. Zhang, *J Mater Chem C*, 2014, 2, 7552-7560.
- 34. L. Bu, M. Sun, D. Zhang, W. Liu, Y. Wang, M. Zheng, S. Xue and W. Yang, *J Mater Chem C*, 2013, 1, 2028-2035.
- X. Sun, X. Zhang, X. Li, S. Liu and G. Zhang, J Mater Chem, 2012, 22, 17332-17339.
- 36. W. Mao, K. Chen, M. Ouyang, J. Sun, Y. Zhou, Q. Song and C. Zhang, *Acta Chim Sinica*, 2013, 71, 613-618.
- H. Zhang, Z. Zhang, K. Ye, J. Zhang and Y. Wang, *Adv Mater*, 2006, 18, 2369-2372.
- 38. K. S. Yook and J. Y. Lee, Adv Mater, 2012, 24, 3169-3190.
- E. W. R. Cristiano, I. H. Bechtold, A. J. Bortoluzzi and H. Gallardo, *Tetrahedron*, 2007, 63, 2851-2858.
- 40. H. Zhao, Y. Wang, Z. Liu and B. Dai, *RSC Adv*, 2014, 4, 13161-13166.
- 41. M. T. Lee, H. H. Chen, C. H. Liao, C. H. Tsai and C. H. Chen, *Appl Phys Lett*, 2004, 85, 3301-3303.

Page 6 of 7

# AIE-active mechanochromic materials based N-phenylcarbazol-substituted tetraarylethene for OLED applications

He Zhao,<sup>a</sup> Yang Wang,<sup>b</sup> Yongtao Wang,<sup>\* a</sup> Gufeng He,<sup>\*b</sup> Mei Xue, <sup>a</sup> Pingan Guo, <sup>a</sup>

Bin Dai,\* <sup>a</sup> Zhiyong Liu <sup>a</sup> and Yu Qi <sup>a</sup>

Table of contents entry



Well-designed AIE-active luminogens as both hole-transporting and light-emitting layer materials can be utilized to fabricate metal free and nondoped OLEDs.