Check for updates

Journal of Materials Chemistry C

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: S. Ying, M. Chen, Z. Liu, M. Zheng, H. Zhang, S. Xue and W. Yang, *J. Mater. Chem. C*, 2017, DOI: 10.1039/C7TC01453H.

Volume 4 | Number 1 | 7 January 2016 | Pages 1–224

Journal of Materials Chemistry C

Materials for optical, magnetic and electronic devices
www.rsc.org/MaterialsC

ISSN 2050-7526

ROYAL SOCIETY OF CHEMISTRY

PAPER
Nguyễn T. K. Thanh, Xiaodi Su et al.
Fine-tuning of gold nanorod dimensions and plasmonic properties using the Hofmeister effects

175 YEARS

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. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the author guidelines.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the ethical guidelines, outlined in our author and reviewer resource centre, 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.

ROYAL SOCIETY OF CHEMISTRY

rsc.li/materials-c

Please do not adjust margins

View Article Online
DOI: 10.1039/C7TC01453H

Journal Name

ARTICLE

Published on 12 May 2017. Downloaded by Freie Universitaet Berlin on 13/05/2017 16:37:54.

Journal of Materials Chemistry C Accepted Manuscript

Unusual Mechanohypsochromic Luminescence and Unique Bidirectional Thermofluorochromism of Long-Alkylated Simple DPP Dyes

894Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Shian Ying, Mingshuai Chen, Zhongwei Liu, Meng Zheng, Haichang Zhang, Shanfeng Xue,* and Wenjun Yang*

There have been hundreds of organic and metallorganic compounds found to exhibit mechanobathochromic luminescence within tens of nanometers. This paper presents the first example of unusual mechanohypsochromic luminescence and unique bidirectional thermofluorochromism based on 1,4-diketo-2,5-di(tetradecyl)-3,6-bis-(4-chlorophenyl)pyrrolo[3,4-c]pyrrole (TDPP). Pristine TDPP powder is a red emitting crystal (645 nm, R state) and can be changed into a yellow amorphous state (544 nm, Y state) by mechanical grinding or solution spin-coating. The Y state could revert to R state upon annealing below 60 ^{o}C or solvent-fuming, however, annealing the Y state above 70 ^{o}C produces a new green-emitting crystalline state (523 nm, G state). Moreover, the G state can transform to Y and R states upon grinding and solvent-fuming, respectively. In contrast, those novel phenomena are not observed in the butylated DPP, demonstrating that peripheral alkyl chain lengths of organic fluorophores can play the diverse functional role in determining the solid-state aggregation behavior and fluorescence properties. This work has enriched kinds of stimuli responsive materials and developed new optical properties of alkylated DPPs.

Introduction

Stimuli-response fluorescent solids exhibiting the reversible change in emission colour or intensity upon external stimuli such as light irradiation,[1] chemical vapor,[2] heat treatment,[3] and mechanical force,[4] etc. have attracted much attention due to their potential applications in various sensors and optical recording and academic importance in understanding photo-physical properties. Among them, mechanofluorochromic (MFC) materials involving the physical change of aggregate morphology instead of the chemical structure alteration have drawn much interest only within the past decade because of the easy realization and materials diversity.[4,5] However, there are still no rational design strategies for MFC dyes since almost the identified MFC dyes are isolated events, and it is hard to predict in advance whether a newly synthesized fluorescent molecule can exhibit MFC behaviour. Therefore, there is still a great demand on experimental exploitation of new MFC dyes and accumulation of structure–property relationships. In this context, the design and discovery of MFC materials with simple and comparable chemical structures are interesting but still scarce at present. Moreover, although there have been hundreds of organic and metallorganic compounds found to exhibit MFC behaviour, almost the present MFC dyes are characterized by mechanobathochromic shift within tens of nanometers,[4,5] and those with high contrast, multicolour and multichannel switching are limited.[6] Further, to the best of our knowledge, organic fluorescent dyes exhibiting remarkable mechanohypsochromic luminescence are rarely realized.[7]

In recent years, we and others[8,9] have found that the solid-state optical and electronic properties and stimuli-response behaviours of some organic chromophores are significantly related to the positions and lengths of peripheral alkyl chains, which has demonstrated the important role of flexible side chains in tuning the molecular aggregation behaviours and triggered the research of ‘‘side-chain engineering’’ or “homologous effect”. We are now interested in 3,6-bis(aryl)-1,4(*2H,5H*)-diketo-pyrrolo[3,4-c]pyrroles (DPPs) because DPPs represent a class of commercial high-performance pigments, and insoluble DPP pigments can be changed into highly soluble and fluorescent dyes by introducing alkyl chains on the lactam moiety to eliminate strong intermolecular hydrogen bonds. While alkylated DPPs have been widely used in building promising field-effect transistor and photovoltaic materials and fluorescent probes,[10] their solid fluorescence and stimuli-response properties are rarely investigated. We consider that changing peripheral alkyl lengths of DPPs should tune the

Key Laboratory of Rubber-Plastics of Ministry of Education/Shandong Province (QUST), School of Polymer Science & Engineering, Qingdao University of Science & Technology, 53-Zhengzhou Road, Qingdao 266042, P. R. China, E-mail: sfxue@qust.edu.cn, ywjph2004@qust.edu.cn

†Electronic Supplementary Information (ESI) available: The detail of experimental section; detailed absorption and emission spectra of compounds in different solvents; fluorescence images and spectra of TDPP and BDPP solids under various external stimuli; molecular packing structures and π-backbone conformations of BDPP and TDPP. See DOI: 10.1039/x0xx00000x

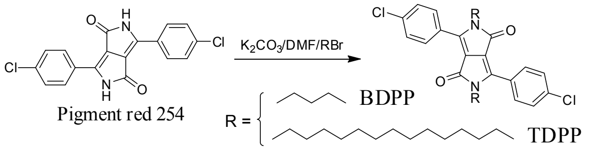
This journal is © The Royal Society of Chemistry 20xx

View Article Online
DOI: 10.1039/C7TC01453H

Published on 12 May 2017. Downloaded by Freie Universitaet Berlin on 13/05/2017 16:37:54.

Journal of Materials Chemistry C Accepted Manuscript

intermolecular π–π and the aliphatic–aliphatic interactions, which probably varies molecular conformations and packing modes to allow the design of functional dyes with polymorphs and unique stimuli-response behaviours. Thus here we have introduced a short (butyl) and a long (tetradecyl) alkyl chains at the 2,5-positions of commercial Pigment Red 254 to obtain two soluble DPP derivatives (BDPP and TDPP, **Scheme 1**). It was surprisingly found that both the TDPP solid powder and the spin-coated film exhibited unusual mechanohypsochromic luminescence with large spectral shift up to 100 nm and unique bidirectional thermochromism depending on annealing temperature. This is the first example of such MFC materials, and stimuli responsive materials are enriched and optical properties of alkylated DPPs are developed.



Scheme 1. Structure and synthetic route of DPP dyes studied here.

Results and discussion

Both BDPP and TDPP solutions emit yellow fluorescence (~542 nm), regardless of solvent polarity and alkyl length, except for slightly changed fluorescence quantum yield (36~47%, **Figure S1 and Table S1**). BDPP solid is an orange emitting (600 nm) and non-MFC active crystal with the fluorescence efficiency of 25.8% (**Figure S2**). However, TDPP can form two fluorescence colour solids from the same solution, depending on solvent-evaporation way or rate (**Figure 1**). When solvent is removed using routine rotary evaporator, a red-emitting crystalline powder (645 nm, R state) with the moderate fluorescence efficiency of 14.8% is obtained. In contrast, spin coating (3000 rpm) the solution on a quartz plate affords a yellow film with the fluorescence efficiency of 5.6% (Y state, top in **Figure 1 and Figure S3a**). This Y state exhibits a broad emission with two peak-wavelengths of 530 and 560 nm. R and Y states are all stable under common ambient conditions, but R state can convert to Y state by mechanical grinding using a metal spatula on a glass plate at room temperature (RT). Moreover, the Y state can easily change back to R state upon exposing to solvent vapour at RT within a few minutes (**Figure 1**). The grinding- and spin coating-induced Y states show the similar fluorescence colours and emission spectra with the central wavelength of 544 nm. Compared to absorption spectra of the pristine spin-coating film, the G state film has a slight blue-shift. And R state film have a strong red-shift from 458 nm to 578 nm (**Figure S3a**).The above fluorescence change process is repeatable and indicates a reversible MFC behaviour. Notably, the grinding-induced spectral shift (~100 nm) is not only among the largest values reported to date, but also unique rare mechanohypsochromic shift.

To our surprise once again, when the Y state is gently annealed at 40 °C, the red and green regions appear simultaneously and unevenly on the sample surface even if annealing time is extended to 30 hours (**Figure S3b**). It would seem that the Y state could form the two different thermochromic states. Thus, we increase the annealing temperature to 50–68 °C, and find that the Y state is eventually turned into the R state within a few hours (**Figure 1**, **Figure S3b** and **S3c**). Interestingly, if the annealing temperature rises to 70–90 °C, a strong green-emitting state (523 nm, G state) without any red spot is obtained within minutes (**Figure 1 and Figure S3**) . Therefore, we think 70 °C is the favorable temperature that Y state could be turned into G state. The G state has a higher fluorescence efficiency of 29.5% and shows a narrower emission spectrum. The R and G states form once, they are all thermodynamically stable and can not transform each other by thermal annealing before isotropic melt transition, but G state can convert to R state by solvent-fuming or change into Y state by mechanical grinding.

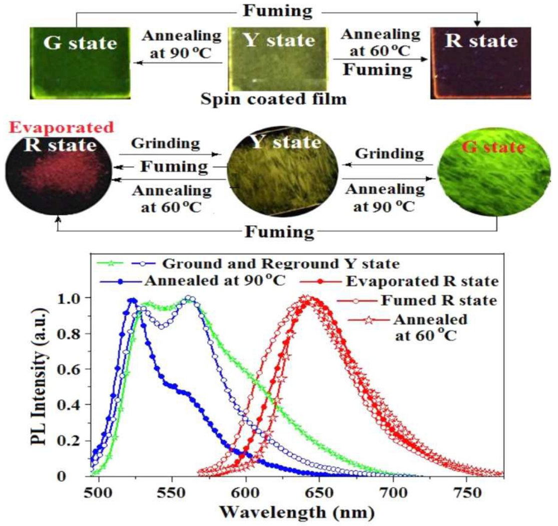


Figure 1. Fluorescence images (top, illuminated by 365 nm UV lamp) and spectra (down) of TDPP solids under various external stimuli. The spectra are excited at 480 nm.

Thermal analysis indicates that TDPP exhibits the complex but interesting thermal properties (**Figure 2**). DSC shows that R state performs a dominant isotropic melting transition at 98 °C upon heating process, and the melt can crystallize at ~50 °C upon cooling process. Heating the cooled melt (second heating) produces a broad exothermic peak at 30–40 °C and a higher isotropic melting transition at 106 °C. The appearance of the exothermic peak implies incompleteness of melt crystallization and relaxation of the molecular motion, and the incomplete crystals can take place cold crystallization upon heating to afford an exothermic peak. It is found that the isotropic melt hardly fluoresces. We could obtain a yellow-emitting solid by cooling the melt in outage oven, and its emission spectrum and stimuli response behaviours are same as above Y state (**Figure S5**). Thermal analysis indicates that Y state also has a broad exothermic peak at 30–40 °C (**Figure 2**), an amorphous feature. Isothermally cooling the melt (in 45 °C oven) forms a green-emitting solid, and its emission spectrum and stimuli

This journal is © The Royal Society of Chemistry 20xx

Please do not adjust margins

View Article Online
DOI: 10.1039/C7TC01453H

Published on 12 May 2017. Downloaded by Freie Universitaet Berlin on 13/05/2017 16:37:54.

Journal of Materials Chemistry C Accepted Manuscript

response behaviours are same as above G state (**Figure S5**). The G state shows no cold crystallization peak upon heating and only a isotropic melting transition at 106 $^{\circ}$C, indicative of its well-ordered crystalline nature. Overall, G state is more thermodynamically stable, and R state is more kinetically preferred.

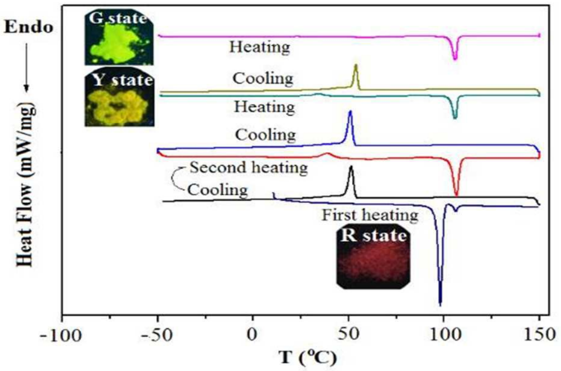


Figure 2. DSC curves of TDPP solids prepared from the different conditions. The insets are the fluorescence images illuminated by a 365 nm UV lamp.

Cross-polarized optical microscopy displays that both R and G states are crystalline, and both spin-coated and grinding-induced Y states show amorphous characteristics (top inset, **Figure 3**). Thus, MFC behaviour of TDPP solid could be ascribed to the phase transition between crystalline and amorphous states upon external stimuli. Powder X-ray diffraction patterns further confirm that R and G states are in well-ordered but very different crystalline states (**Figure 3**), and the obtained Y state by cooling the melt is a hybrid state of semi-crystalline and certain amorphous characteristics. However, cooling the melt in room air could form a quasi Y state with more obvious amorphous characteristics. It could be considered that flash solvent-evaporation (spin coating) and fast melt-cooling (in air) would make the long alkyl DPP molecules with relaxation feature fail to packing in a well orderly manner, but the local ordered structures could still be formed (quasi Y state). Grinding the R and G states could leave the residual crystal seeds, thus, upon solvent-fuming and heat-annealing, the molecular secondary motions are effectively stimulated and the well-ordered crystalline states are formed.

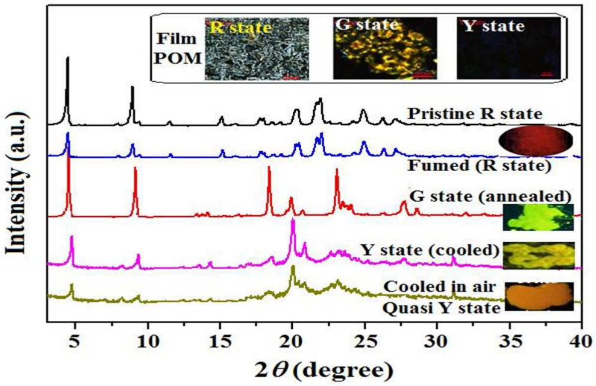


Figure 3. Powder x-ray diffraction patterns of TDPP solids prepared under different conditions. Top inset is the cross-polarized optical microscopic photos of TDPP film.

To further gain an insight into the different solid-state fluorescence properties of alkyl DPPs, we have cultured and analyzed single crystal structures of BDPP and TDPP (**Figure 4 and Figure S6, Table S2 and S3**).[10] In the orange BDPP crystal, the molecule has a non-planar DPP core with a dihedral angle of 173.6°, and its two chlorophenyl units are strongly twisted relative to lactam ring with two different dihedral angles of 41.8° and 47.4°, respectively. Two butyl chains are homotropous in DPP out-of-plane and interact weakly. The adjacent BDPP molecules pack in anti-parallel mode with the laterally slipped angle of 19.5° and a vertical distance 3.329 Å. This is a H-aggregation with the strong twisted backbone and less π-π overlap stabilized by the intermolecular phenyl CH---O interactions. In sharp contrast, in the TDPP single crystal with red emission as R state, the molecules have the nearly planar DPP core (179.6°) and less twisted chlorophenyl units (13.5°). The adjacent TDPPs take stretching all-trans alkyl chains to pack in face-to-face parallel with a vertical π–π distance of 3.345 Å and strong aliphatic–aliphatic interactions. One molecule slides to its neighbour along π-backbone long axis (44.1°), affording a J-aggregation mode with the less twisted backbone and large π-π overlap stabilized by strong intermolecular alpha-H---O and π-π inter-actions. Thus, the redder emission for TDPP than BDPP crystals could be ascribed to the former molecules with less twisted π-backbone extending effective conjugation, strong π-π inter-actions facilitating excimer formation, and J-aggregation red-shifting but enhancing emission. In this context, it could be considered that TDPP molecules in Y and G states all have more twisted and bent π-backbones, regardless of different packing modes. It is also reasonable that, to form well-ordered crystal, the long-alkyl molecules should pack in parallel fashion along stretched all-trans alkyl chains, and the intermolecular π-π interactions could be weaker for crystalline G state than crystalline R state. Overall, changing the length of alkyl chains can greatly affect the solid-state aggregation behaviour and fluorescence properties, and the long alkyl chain is more suitable for tuning the intermolecular π–π and the aliphatic–aliphatic interactions to allow the design of functional dyes with polymorphs and unique stimuli-response behaviours.

To further understand the different emissive states formed by TDPP molecules, we have measured their IR spectra (**Figure 4 and S6**). The alkyl stretching (2917, 2848 cm^{-1}) and rocking (723 cm^{-1}) vibrations in R state are respectively blue shifted to 2920, 2851, and 724 cm^{-1} in G state, which implies stronger aliphatic–aliphatic interactions in G state. The C=C stretching (1587, 1578 cm^{-1}) and C–H bending (736, 699 cm^{-1}) for phenyl rings in R state are also blue shifted in G state (1614 and 1588, 740 and 700 cm^{-1}, respectively), indicating more twisted π-skeleton in G state. On the other hand, it is observed that intermolecular phenyl CH–keto interactions in BDPP crystal (distances 2.559 and 2.419 Å) are stronger than that in R state of TDPP (distances 2.987 and 2.786 Å, **Figure S5c**), and the corresponding keto stretching appears at 1680 and 1674 cm^{-1}, respectively (**Figure S6**). In this context, the intermolecular interactions caused by keto moiety would be even weaker in G state since the observed keto stretching vibration for G state

View Article Online
DOI: 10.1039/C7TC01453H

Published on 12 May 2017. Downloaded by Freie Universitaet Berlin on 13/05/2017 16:37:54.

appears only at 1663 cm^{-1}. Different molecular π-backbone conformations and intermolecular interactions for G and R states could also be evidenced by other attribute-unknown peaks, for example, two peaks at 848 and 833 cm^{-1} existed in G state disappear in R state, instead, two new peaks at 831 and 772 cm^{-1} appear. As for Y state, the IR spectrum is similar to that of G state (**Figure S6**), which could be ascribed to their resembled emission spectra and x-ray diffraction patterns.

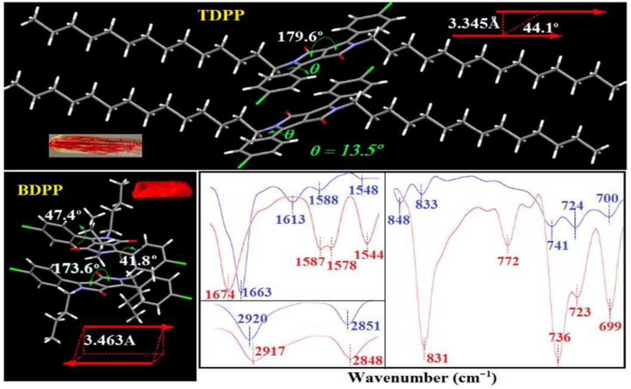


Figure 4. Adjacent molecular packing π-backbone angle od alkyl DPPs and IR screenshots of G state (blue line) and R state (red line) of TDPP film (lower right corner).

Conclusions

We have demonstrated that alkylating simple commercially available DPP pigments can obtain multi-functional fluorescent dye, and alkyl DPPs have become a new class of "side-chain engineering" systems. While there have been hundreds of organic and metallorganic compounds exhibiting mechano-bathochromic luminescence, this work has presented the first example of large mechanohypsochromic luminescence. Thus, the kinds of stimuli responsive dyes are enriched and new optical properties of alkyl DPPs developed. Only long-alkylated DPPs could exhibit unusual mechanochromic and unique thermochromic multi-colour luminescence, emphasizing the important role of long alkyl chain in tuning π–π and aliphatic–aliphatic interactions and obtaining polymorphs and diverse optical properties. This finding could arouse one's further attention to the alkyl length effect in design, synthesis and structure–property investigation of organic optoelectronic materials. It is possible that utilizing this strategy design new functional dyes based on other small organic chromophores, and further extensive and systematic research is underway.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (51473084, 51573081) and the Natural Science Foundation of Shandong Province (No. ZR2016JL016, ZR2014EMQ013), and the Natural Science Foundation of Qingdao City of China (16-5-1-89-jch). We thank Open Project of the State Key Laboratory of Supramolecular Structure and Materials of Jilin University (SKLSSM-201728).

Notes and references

1 J. W Chung, Y. You, H. S. Huh, B.-K. An, S.-J. Yoon, S. H. Kim, S. W. Lee, and S. Y. Park, *J. Am. Chem. Soc.*, 2009, **131**, 8163.

2 K. Wang, S. Huang, Y. Zhang, S. Zhao, H. Zhang, and Y. Wang, *Chem. Sci.*, 2013, **4**, 3288.

3 (a) Y. Zhao, H. Gap, Y. Fan, T. Zhou, Z. Su, Y. Liu, and Y. Wang, *Adv. Mater.*, 2009, **21**, 3165; (b) T. Mutai, H. Satou, and K. Araki, *Nat. Mater.*, 2005, **4**, 685.

4 (a) Y. Sagara, and T. Kato, *Nat. Chem.*, 2009, **1**, 605; (b) Z. Chi, X. Zhang, B. Xu, X. Zhou, C. Ma, Y. Zhang, S. Liu, and J. Xu, *Chem. Soc. Rev*., 2012, **41**, 3878; (c) Y. Q. Dong, J. W. Y. Lam, and B. Z. Tang, *J. Phys. Chem. Lett.*, 2015, **6**, 3429; (d) Z. Mao, Z. Yang, Y. Mu, Y. Zhang, Y. Wang, Z. Chi, C. Lo, S. Liu, A. Lien, and J. Xu, *Angew. Chem. Int. Ed.,* 2015, **54**, 6270. (e) B. Xu, J. He, Y. Mu, Q. Zhu, S. Wu, Y. Wang, Y. Zhang, C. Jin, C. Lo, Z Chi, A. Lien, S. Liu, and J. Xu, *Chem. Sci.*, 2015, **6**, 3236–3241; (f) S. Saito, H. Yusa, H. Yamawaki, H. Fujihisa, H. Sato, Y.Shimoikeda, and S. Yamaguchi, *J. Am. Chem. Soc.*, 2013, **135**, 10322-10325; (g) R. Li, S. Xiao, Y. Li, Q. Lin, R. Zhang, J. Zhao, C. Yang, K. Zou, D. Li, and T. Yi, Chem. Sci., 2014, **5**, 3922–3928; (h) R. Tan, Q. Lin, Y. Wen, S. Xiao, S. Wang, R. Zhang and T. Yi, *CrystEngComm*, 2015, **17**, 6674-6680.

5 (a) T. Seki, Y. Takamatsu, and H. Ito, *J. Am. Chem. Soc.*, 2016, **138**, 6252; (b) J. Kunzelman, M. Kinami; B. R. Crenshaw, J. D. Protasiewicz, and C. Weder, *Adv. Mater.*, 2008, **20**, 119; (c) S. Y. Yoon, J. W. Chung, J. Gierschner, K. S. Kim, M. G. Choi, D. Kim, and S. Y. Park, *J. Am. Chem. Soc.*, 2010, **132**, 13675; (d) Y. Dong, B. Xu, J. Zhang, X. Tan, L. Wang, J. Chen, H. Lv, S. Wen, B. Li, L. Ye, B. Zou, and W. Tian, *Angew. Chem. Int. Ed.*, 2012, **51**, 10782; (e) X. Luo, J. Li, C. Li, L. Heng, Y. Dong, Z. Liu, Z. Bo, and B. Tang, *Adv. Mater.*, 2011, **23**, 3261; (f) S. Yagai, S. Okamura, Y. Nakano, M. Yamauchi, K. Kishikawa, T. Karatsu, A. Kitamura, A. Ueno, D. Kuzuhara, H. Yamada, T. Seki, and H. Ito, *Nat. Commun.*, 2014, **5**, 4013.

6 (a) W. Z. Yuan, Y. Q. Tan, Y. Y. Gong, P. Lu, J. W. Y. Lam, X. Y. Shen, C. F. Feng, H. H. Y. Sung, Y. W. Lu, I. D. Williams, J. Z. Sun, Y. M. Zhang, and B. Z. Tang, *Adv. Mater.*, 2013, **25**, 2837; (b) Y. Sagara, and T. Kato, *Angew. Chem. Int. Ed.*, 2011, **50**, 9128. (c) M. Okazaki, 0. Takeda, P. Data, P. Pander, H. Higginbotham, A. P. Monkman, and S. Minakata, *Chem. Sci*., DOI: 10.1039/c6sc04863c. (d) Q. Sui, X.-T. Ren, Y.-X. Dai, Kai Wang, W.-T. Li, T. Gong, J.-J. Fang, B. Zou E.-Q. Gao, and L. Wang, Chem. Sci., DOI: 10.1039/c6sc04579k. (e) Y. Jiang , D. Gindre, M. Allain, P. Liu, C. Cabanetos, and J. Roncali, *Adv. Mater*., 2015, **27**, 4285.

7 (a) M. Tanioka, S. Kamino, A. Muranaka, Y. Oyama, H. Ota, Y. Shirasaki, J. Horigome, M. Ueda, M. Uchiyama, D. Sawada, and S. Enomoto, *J. Am. Chem. Soc.*, 2015, **137**, 6436; (b) Y. Sagara, K. Kubo, T. Nakamura, N. Tamaoki, and C. Weder, *Chem. Mater*., 2017, **29**, 1273.

8 (a) Y. Wang, T. Liu, L. Bu, J. Li, C. Yang, X. Li, Y. Tao, and W. Yang, *J. Phys. Chem. C*, 2012, **116**, 15576; (b) X. Zhang, Z. Chi, B. Xu, L. Jiang, X. Zhou, Y. Zhang, S. Liu, and J. Xu, *Chem. Commun.*, 2012, **48**, 10895; (c) S. Xue, X. Qiu, Q. Sun, and W. Yang, *J. Mater. Chem. C*, 2016, **4**, 1568.

9 (a) J. Mei, and Z. Bo, *Chem. Mater.*, 2014, **26**, 604; (b) F. Zhang, Y. Hu, T. Schuettfort, C. Di, X. Gao, C. R. McNeill, L. Thomsen, S. Mannsfeld, W. Yuan, H. Sirringhaus, and D. Zhu, *J. Am. Chem. Soc.*, 2013, **135**, 2338.

10 (a) L. Dou, Y. Liu, Z. Hong, G. Li, and Y. Yang, Chem. Rev., 2015, **115**, 12633; (b) W. Li, K. H. Hendriks, M. M. Wienk, and R. A. Janssen, *J. Acc. Chem. Res.*, 2016, **49**, 78; (c) M. Kaur, and D. H. Choi, *Chem. Soc. Rev.*, 2015, **44**, 58.

11 CCDC 1497296 and 1497297 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Journal of Materials Chemistry C Accepted Manuscript

View Article Online
DOI: 10.1039/C7TC01453H

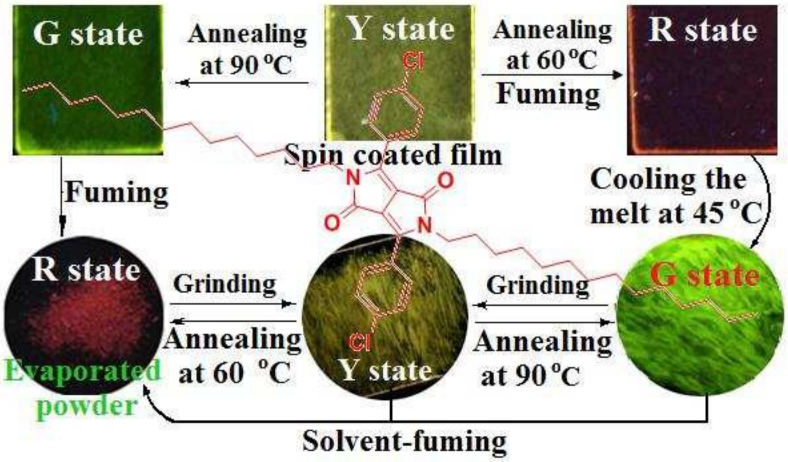
Published on 12 May 2017. Downloaded by Freie Universitaet Berlin on 13/05/2017 16:37:54.

Journal of Materials Chemistry C Accepted Manuscript

Unusual Mechanohypsochromic Luminescence and Unique Bidirectional Thermofluorochromism of Long-Alkylated Simple DPP Dyes

Shian Ying, Mingshuai Chen, Zhongwei Liu, Meng Zheng, Haichang Zhang, Shanfeng Xue,* and Wenjun Yang*

Key Laboratory of Rubber-plastics of Ministry of Education/Shandong Province (QUST), School of Polymer Science & Engineering, Qingdao University of Science &Technology, 53-Zhengzhou Road, Qingdao, 266042, P. R. China. E-mail: sfxue@qust.edu.cn, ywjph2004@qust.edu.cn



The first example of organic dyes exhibiting very large mechanohypsochromic shift (~100 nm) and bidirectional thermofluorochromism (red, yellow, and green) in both powder and film states was demonstrated based on a long-alkylated Pigment Red 254 (TDPP). Thus, the kinds of stimuli responsive dyes are enriched and new optical properties of alkyl DPPs developed.