

View Article Online View Journal

ChemComm

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: N. Xie, C. Li, J. Liu, W. Gong, B. Z. Tang, G. Li and M. Zhu, *Chem. Commun.*, 2016, DOI: 10.1039/C6CC01187J.



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 **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/chemcomm

Published on 24 March 2016. Downloaded by University of California - San Diego on 24/03/2016 10:07:42.

Terrylenediimide-Tetraphenylethene Dyads[†]

COVAL SOCIETY

Journal Name

COMMUNICATION



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

Nuo-Hua Xie,^a Chong Li, *^a Jun-Xia Liu,^a Wen-Liang Gong,^a Ben Zhong Tang,*^b Guigen Li,*^c and Ming-Qiang Zhu*^{a,c}

Synthesis and Aggregation-Induced Near-Infrared Emission of

DOI: 10.1039/x0xx00000x

www.rsc.org/

We design and synthesize terrylenediimide-tetraphenylethene dyads, which exhibit featured aggregation-induced near-infrared fluorescence with maximum emission wavelength up to 800 nm.

Perylenediimides and terrylenediimides have been used as long-wavelength (red or near-infrared) emissive molecules in organic optoelectronics and biosensing because of their high efficient emission in dilute organic solution.^{1,2} However, their applications have been limited because the strong aggregation tendency of planar perylenediimides and terrylenediimides in concentrated solution or in solid state causes dramatic fluorescence quenching.³ Although they emit intensely in dilute solutions, their light emissions are often guenched when they are fabricated into solid films due to compact aggregate formation, resulting in distinct drop of luminescence efficiency.⁴ They are also highly susceptible to concentration quenching and become either weakly emissive or even not emissive at all in solid state.⁵ The limitation can promisingly be broken by introducing aggregation induced emission (AIE). AIE was discovered in 2001,⁶ and within the last few years a great deal of effort has been undertaken to study this phenomenon.⁷⁻⁸ AIE-active materials such as silole⁹ and tetraphenylethene,¹⁰ are chromophores that exhibit fluorescence quenching in the solution, contrary to it solid state, which shows enhanced luminescence. Tetraphenylethene (TPE) was selected as an ideal fluorophore due to its large Stokes' shifted fluorescence as well as enhanced fluorescence in solid state than in solution.¹¹ Previous investigations indicate that PDI-TPE conjugates show their typical aggregation-induced red emission.¹²⁻¹⁴ Taking

advantage of the attractive properties of TPE and since it can be easily modified as a molecular building block, it would be desirable to design terrylenediimide-tetraphenylethene conjugates (TDI-TPEs) enabling condensed state enhanced near-infrared emission. Recently, aggregation induced nearinfrared emission materials aroused great attentions due to their good prospect in optoelectronic and biological areas.¹⁵ Although several works in literatures have reported AIE luminogens with far red/near-infrared emission, their maximum emission peaks were usually located below 700nm or only part of their emission spectra was spread into the NIR range.^{13,16-18} Besides, many of them rely on an elaborate design and complex synthesis.^{19,20} Here we integrate TDI and AIEactive TPE into a single molecule by covalently binding one TDI and four TPE molecules. We designed two styles of covalent binding: one is π -conjugated (TDI-4TPE) while another is Obridged non-conjugated (TDI-O-4TPE). By this way, TDI as a typical aggregation-induced quenching (ACQ) fluorophore was converted to NIR-AIE luminogens exhibiting characteristic aggregation-induced enhanced near-infrared fluorescence with maximum emission wavelength up to 800 nm which has not have been reported before to the best of our knowledge.



Scheme 1 Synthetic route to TDI-4TPE and TDI-O-4TPE conjugates

^{a.} Wuhan National Laboratory for Optoelectronics, School of Optical and Electronic Information, Huazhong University of Science and Technology, Wuhan, Hubei, 430074, China, E-mail: mqzhu@hust.edu.cn, chongli@hust.edu.cn; Fax: +86-27-87793419.

^{b.} Department of Chemistry, The Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong. E-mail: Tangbenz@ust.hk.

^{c.} Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409–1061, United States. E-Mail: guigen.li@ttu.edu.

⁺ Electronic Supplementary Information (ESI) available: experimental procedures/characterization, optical spectra, and molecular simulation. See DOI: 10.1039/x0xx00000x

Published on 24 March 2016. Downloaded by University of California - San Diego on 24/03/2016 10:07:42.

DOI: 10.1039/C6CC01187J Journal Name



Fig. 1 HOMO and LUMO energy levels of (a) TDI-4TPE and (b) TDI-0-4TPE. Molecular orbital amplitude plots of HOMO and LUMO energy levels calculated using B3LYP/6-31G (d) basis set in Gaussian 09program. E_g (energy gap) = LUMO -HOMO.

The synthetic procedures of TDI-4TPE and TDI-O-4TPE are shown in Scheme 1. TDI-4TPE was synthesized by Suzuki cross-coupling of TDI-4Br with TPE-B(OH)₂. TDI-O-4TPE was prepared by nucleophilic substitution of TPE-OH with TDI-4Br in the presence of K₂CO₃. TDI-4TPE and TDI-O-4TPE were produced with practical yields, and exhibit good solubility in common solvents. The detailed synthetic procedures are depicted in electronic supplementary information (ESI⁺). The final products were fully characterized by ¹H NMR, ¹³C NMR, MALDI-TOF, HPLC (Fig. S1, ESI⁺), element analysis and correspond well with their expected structures (See the ESI⁺).

TDI-4TPE and TDI-O-4TPE have donor-acceptor (D–A) structures, which contain elementary units of electrondonating TPE and electron-accepting TDI. The only difference of TDI-4TPE and TDI-O-4TPE is that there is charge transfer from TPEs to TDI due to the electron conjugation between TDI and TPEs in TDI-4TPE while that of TDI-O-4TPE has been isolated by O-bridges. Density functional theory (DFT)

calculations of TDI-4TPE and TDI-O-4TPE were carried out to understand their geometries and electronic structures at the molecular level. The optimized geometries of TDI-4TPE and TDI-O-4TPE are shown in Fig. 1a and 1b, respectively. Both TDI-4TPE and TDI-O-4TPE embrace twisted conformations along the backbone compared with planar structure of TDI (Fig. S2, ESI⁺). The computerized energy gap (Eg) of TPE, TDI, TDI-4Br, TDI-4TPE and TDI-O-4TPE are 4.12, 1.98, 2.01, 1.79 and 1.87eV, respectively. The twisting angles between the naphthalene units in central terrylene plane are 21.66° for TDI-4TPE while that of TDI-O-4TPE is 16.17°. The dihedral angles between the two outermost naphthalene units are 54.18° in TDI-4TPE. Evidently, strong torsion between naphthalene units in TDI-4TPE results from the steric effect and electron conjugation of adjacent TPEs. Such propeller-like, non-planar conformations of these two molecules, especially for TDI-4TPE, would severely impede the π - π stacking interactions between terrylene units in the aggregate state. In terms of the electronic structures, the lowest unoccupied molecular orbitals (LUMO) of TDI-4TPE is dominated by the orbitals from the TDI core, while the electron cloud of the highest occupied molecular orbitals (HOMO) is stretched to TPE units. The HOMO-LUMO distribution indicates that TDI-4TPE possesses an intrinsic intramolecular charge transfer (ICT) character. In comparison, the LUMO and HOMO of TDI-O-4TPE are not apparently influenced by introduction of four TPE units.



Fig. 2 Optical properties in organic solvents. (a) Absorption and (b) Fluorescence spectra of TDI-4TPE. (c) Absorption and (d) Fluorescence spectra of TDI-0-4TPE. (e) and (f) are the fluorescence decay curves of TDI-4TPE and TDI-0-4TPE respectively. For the steady-state spectra, the excitation wavelength is 600nm. The solutions were prepared by injecting of 25 μ L DCM solution (1 × 10⁻³ M) into 2.5 mL different organic solvents. Each the organic solvent contains 1% DCM. Especially, the dye molecules are aggregated as nanoparticles in poor solvents such as hexane, methanol and DMF. For the transient state fluorescence spectra, the excitation wavelength is 340 nm and the maximum emission wavelengths

Journal Name

were monitored. The instrument response function (IRF) is about 100 ps. The concentrations for all the solutions are 1×10^{5} M.



Fig. 3 Optical properties of TDI-4TPE and TDI-O-4TPE in hexane/DCM binary solvents with different hexane fractions (by volume %). (a) Absorption and (b) fluorescence spectra of TDI-4TPE (c) Absorption and (d) fluorescence spectra of TDI-0-4TPE. The concentrations are all 1.0×10^{-5} M.The excitation wavelength is 600nm.

We investigated the optical properties of TDI-4TPE and TDI-O-4TPE in various organic solvents. The corresponding UV-Vis absorption and emission spectra are presented in Fig. 2. The absorption spectra of TDI-4TPE and TDI-O-4TPE in dichloromethane (DCM) are peaked at ~731 and ~697 nm, respectively, indicative of a longer conjugation length of TDI-4TPE due to the integration of four TPEs (Fig. 2a and 2c). The decreases of the absorbance of TDI-O-4TPE in DMF and methanol are attributed to the poor solubility of high hydrophobic molecules in strong polar solvents. The molar absorptivity of TDI-4TPE (6.46 × 10⁴ M⁻¹ cm⁻¹) is similar to that of TDI-O-4TPE (7.27 × 10⁴ M⁻¹ cm⁻¹).

TDI-4TPE and TDI-O-4TPE have considerable fluorescence quantum yields (QYs) in low polar solvents while relatively lowin polar solvent (Table S1). Their fluorescence lifetimes (Fig. 2e and 2f, Table S2) decrease as the polarity increase indicating that the non-radiative transitions process are strengthened and thus the emission become weak. Both λ_{abs} and λ_{em} exhibit considerable redshifts as the solvents varying from weak polar solvent to strong polar solvent. The maximum fluorescence emission peaks (λ_{em}) of TDI-4TPE and TDI-O-4TPE in DCM are present at 797 nm and 718 nm respectively which fall in typical first NIR window (Fig. 2b and 2d). As shown in Fig. 2b (insert picture), the fluorescence of TDI-4TPE is not observable in naked eyes, even in *n*-hexane and cyclohexane because TDI-4TPE completely emits no visible fluorescence but strong NIR fluorescence. In comparison, the "red-edge" fluorescence of TDI-O-4TPE can be seen in naked eyes under 365nm irradiation.

TDI-O-4TPE shows noticeable visible light to far-red absorption and red light to NIR emission. In comparison, the absorption and emission spectra as well as the photos of TDI-4TPE demonstrate that TDI-4TPE shows weak visible light absorption with a little "red-edge" and totally no visible light emission. Alternately, TDI-4TPE shows strong NIR absorption and NIR emission. This indicates that TDI-4TPE is a promising candidate for visible-light transmissive materials with NIR absorption and emission activities which is exactly a NIR fluorescent probe for *in vivo* imaging.



Fig. 4 Optical properties in polystyrene (PS) film. (a) Absorption spectra of TDI. (b) Emission spectra of TDI. (c) Absorption spectra of TDI- 4TPE. (d) Emission spectra of TDI- 4TPE. (e) Absorption spectra of TDI-0-4TPE. (f) Emission spectra of TDI-0-4TPE. Excitation wavelength: 620 nm. The Polystyrene (PS) film samples were prepared by spin coating of chloroform solution containing PS polymer (100 mg/mL) and dyes (0.1 mg/mL, 0.5 mg/mL, 1 mg/mL, respectively) onto clean quartz plates.

The AIE properties of TDI-4TPE and TDI-O-4TPF were investigated in DCM/hexane binary solvents (Fig. 4) as well as THF/water ones (Fig. S3, ESI⁺). The absorption spectra of TDI-4TPE do not show much change with an increase of hexane fraction (Fig. 3a). However, the PL intensity of TDI-4TPE in DCM/hexane is dramatically enhanced as the hexane fraction increase from 10% to 99% (Fig. 3b). For TDI-O-4TPE, the absorbance are fluctuating in a small range when the hexane fraction is between 0-70% and decrease dramatically when the hexane fraction increases to 80%, which is attributed to the poor solubility of TDI-O-4TPE in hexane (Fig. 3c). The photoluminescence (PL) intensity of TDI-O-4TPE exhibits a gradual increase as the hexane fraction in DCM/hexane increases to 70% followed by a drop when hexane is up to 80%, which is probably attributed to the precipitation of TDI-O-TPE from hexane due to the decrease of solubility of TDI-O-TPE in hexane (Fig. 3d). However, their PL intensities decrease with increasing water fraction in THF/water (Fig. S3 and S4, ESI⁺). TDI-4TPE and TDI-O-4TPE exhibit similar AIE characteristics in DCM/hexane although they do not show AIE in THF/water, which are similar to PDI-TPE reported previously.¹²

Since TDI-O-4TPE and TDI-4TPE display AIE-active far-red and NIR activity, their optical properties in polymer matrix have been investigated. The preliminary comparison of the emission spectra of solid powders of TDI, TDI-4Br, TDI-4TPE and TDI-O-4TPE indicates that TDI-4TPE and TDI-O-4TPE emit strong fluorescence while the emission intensities of TDI and

COMMUNICATION

ChemComm Accepted Manuscript

DOI: 10.1039/C6CC01187J Journal Name

4Br-TDI are much weaker (Fig. S4, ESI⁺). It is noteworthy that TDI-4TPE and TDI-O-4TPE do not show evident fluorescent quenching in the solid state due to aggregation-caused



Fig 5 The fluorescence intensity of dyes in PS film under persistent 302 nm UV light irradiation. The monitored emission wavelength: TDI, 670nm; TDI-0-4TPE, 700nm; TDI-4TPE, 780nm; (d) 4-dicyanomethylene-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran, 630nm.

quenching. The absorption spectra of TDI, TDI-4TPE and TDI-O-4TPE in PS films indicate a great linear increase of absorbance at different content in solid PS films (Fig. 4a, 4c and 4e). In the emission spectra, it is observed that the emission intensity of TDI at 0.5 mg/ml is only 1.5-2 times of that of TDI at 0.1 mg/ml (Fig. 4b). Even the first emission intensity of TDI at 1 mg/ml becomes lower than that at 0.5 mg/ml, which indicates that strong aggregation-causing fluorescence quenching at high concentration. In comparison, the emission intensity of TDI-4TPE and TDI-O-4TPE increase gradually with the increase of concentration in PS films (Fig. 4d and 4f). The discernible difference between TDI and their TPE derivatives indicates that the aggregation-caused quenching can be efficiently inhibited, even reversed by introduction of TPE groups. The emission wavelength of TDI-O-4TPE is 695 nm, longer than that of TDI at 665 nm while the maximum emission of TDI-4TPE even shifts to 780 nm, which can act as typical NIR emitters. The maximum emission wavelength exhibits ascending redshifts in order of TDI, TDI-O-4TPE and TDI-4TPE, indicating the electron and conjugation effect gradually increases.

Organic fluorescent dyes have been faced the challenge of photostability. Here we compare the emission intensity change of TDI, TDI-4TPE, TDI-O-4TPE and a commercial dye 4-dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran upon 600 nm visible light (Fig. S5, ESI⁺) and 302 nm UV irradiation (Fig. 5). It was observed that the emission intensity of TDI, TDI-4TPE and TDI-O-4TPE keep constant even increase while the commercial dye exhibit serious photobleaching. Specifically, upon 302 nm irradiation, TDI, TDI-4TPE and TDI-O-4TPE exhibit great photostability (Fig. S6, ESI⁺), implying a potential application in ambient environment single-molecule spectroscopy.

In conclusion, we have designed and synthesized two typical TPE-decorated TDI dyads, which exhibit strong aggregationinduced enhanced emission with excellent photostability in the first NIR window. Especially, the maximum emission peak of TDI-4TPE is up to 800 nm. The absorptions at far-red to near-IR region of TDI-4TPE and TDI-O-4TPE are promising in broadening of photo-responsive spectra in solar cells. Moreover, their NIR emission features are desirable in NIR sensing and deep tissue imaging. The further investigation about the NIR absorbers and emitters of TDI-TPEs is underway. These novel AIE-active NIR emitters will become a promising role in NIR OLED and *in vivo* bioimaging.

This work was supported by the National Basic Research Program (973) of China (2015CB755602 and 2013CB922104) and the National Science Foundation of China (NSFC 21474034 and 21174045). We also thank Analytical and Testing Center of Huazhong University of Science and Technology and the Center of Micro-Fabrication and Characterization (CMFC) of WNLO for use of their facilities.

Notes and references

- 1 S. K. Yang, X. Shi, S. Park, S. Doganay, T. Ha and S. C. Zimmerman, J. Am. Chem. Soc. 2011, **133**, 9964-9967.
- 2 C. Jung, B. K. Müller, D. C. Lamb, F. Nolde, K. Müllen and C. Bräuchle, J. Am. Chem. Soc. 2006, **128**, 5283-5291.
- 3 Z.Xu, B. He, J. Shen, W. Yang and M. Yin, *Chem. Commun.* 2013, **49**, 3646-3648.
- 4 Y. Huang, J. Wang and Z. Wei, *Chem. Commun. 2014*, **50**, 8343-8345.
- 5 W. Wang, L.-S. Li, G. Helms, H.-H. Zhou and A. D. Q. Li, *J. Am. Chem. Soc. 2003*, **125**, 1120-1121.
- 6 J. Luo, Z. Xie, J. W. Y. Lam, L. Cheng, H. Chen, C. Qiu, H. S. Kwok, X. Zhan, Y. Liu, D. Zhu and B. Z. Tang, *Chem. Commun.* 2001, 1740-1741.
- 7 Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Soc. Rev. 2011*, **40**, 5361-5388.
- 8 Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Commun. 2009*, 4332-4353.
- 9 B. Z. Tang, X. Zhan, G. Yu, P. P. S. Lee, Y. Liu and D. Zhu, J. Mater. Chem. 2001, **11**, 2974-2978.
- M. P. Aldred, C. Li, G.-F. Zhang, W.-L. Gong, A. D. Q. Li, Y. Dai, D. Ma and M.-Q. Zhu, J. Mater. Chem. 2012, 22, 7515-7528.
- 11 M. P. Aldred, C. Li and M.-Q. Zhu, *Chem. Eur. J. 2012*, **18**, 16037-16045.
- 12 M. P. Aldred, G.-F. Zhang, C. Li, G. Chen, T. Chen and M.-Q. Zhu, *J. Mater. Chem. C* 2013, **1**, 6709-6718.
- 13 Q. Zhao, S. Zhang, Y. Liu, J. Mei, S. Chen, P. Lu, A. Qin, Y. Ma, J. Z. Sun and B. Z. Tang, J. Mater. Chem. 2012, 22, 7387-7394.
- 14 Y. J. Wang, Z. Li, J. Tong, X. Y. Shen, A. Qin, J. Z. Sun and B. Z. Tang, *J. Mater. Chem. C 2015*, **3**, 3559-3568.
- 15 R. Hu, N. L. C. Leung and B. Z. Tang, Chem. Soc. Rev. 2014, 43, 4494-4562
- 16 X. Y. Shen, W. Z. Yuan, Y. Liu, Q. L. Zhao, P. Lu, Y. G. Ma, I. D. Williams, A. J. Qin, J. Z. Sun and B. Z. Tang, *J. Phys. Chem. C* 2012, **116**, 10541-10547
- 17 K. Li, W. Qin, D. Ding, N. Tomczak, J. L. Geng, R. R. Liu, J. Z. Liu, X. H. Zhang, H. W. Liu, B. Liu and B. Z. Tang, *Sci. Rep.* 2013, **3**, 1150.
- 18 W. Qin, K. Li, G. X. Feng, M. Li, Z. Y. Yang, B. Liu and B. Z. Tang, Adv. Funct. Mater. 2014, 24, 635-643.
- 19 J. L. Geng, K. Li, W. Qin, L. Ma, G. G. Gurzadyan, B. Z. Tang and B. Liu, *Small 2013*, 9, 11, 2012-2019
- 20 H. G. Lu, Y. D. Zheng, X. W. Zhao, L. J. Wang, S. Q. Ma, X. Q. Han, B. Xu, W. J. Tian and H. Gao, *Angew. Chem. Int. Ed.* 2016, **55**, 155-159.

This journal is © The Royal Society of Chemistry 20xx