

View Article Online View Journal

# Journal of Materials Chemistry C

## Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: M. Kim, D. R. Whang, J. Gierschner and S. Park, *J. Mater. Chem. C*, 2014, DOI: 10.1039/C4TC01763C.



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/materialsC

## **RSCPublishing**

### COMMUNICATION

## A Distyrylbenzene Based Highly Efficient Deep Red/Near-Infrared Emitting Organic Solid

Cite this: DOI: 10.1039/x0xx00000x

Mina Kim,<sup>a</sup> Dong Ryeol Whang,<sup>a</sup> Johannes Gierschner,<sup>b</sup> and Soo Young Park<sup>\*a</sup>

Received 00th January 2012, Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Published on 15 October 2014. Downloaded by University of Prince Edward Island on 31/10/2014 07:12:38

A highly efficient deep red/near-infrared emitting organic solid based on  $\beta$ -dicyanostyrylbenzene derivative was reported. Structural, spectroscopic, and quantum-chemical analysis rationalizes strategy to achieve bright solid-state emitters.

Journal of Materials Chemistry C

The rational design of highly emissive  $\pi$ -conjugated organic materials in the solid state is an important prerequisite for optimizing various optoelectronic and photonic applications, such as organic light-emitting diodes (OLEDs),<sup>1,2</sup> organic solid-state lasers,<sup>3</sup> and fluorescent sensors.<sup>4,5</sup> In particular, deep red/near-infrared (DR/NIR) solid state emitters found special attention to realize optical probes for bioimaging and biomedical applications.<sup>6</sup> Though a great number of molecules are highly emissive in dilute solution, most of the organic fluorophores suffer from fluorescence quenching in (nano)aggregates or thin films. In fact, while single crystals are less prone to the fluorescence quenching irrespective of their intermolecular arrangement (H- vs. J-aggregates),<sup>7</sup> polycrystalline samples of H-type aggregates often exhibit severe concentration quenching resulting mainly from trapping of the excitons due to small radiative rates and fast exciton diffusion.8 This calls for a careful design of the molecular features to control both intra- and intermolecular properties. To reduce fluorescence quenching, branched and non-planar molecular architecture,<sup>9-12</sup> J-aggregate formation,<sup>13,14</sup> or cross-dipole stacking<sup>15</sup> have been utilized.

DR/NIR solid state emitters are intrinsically narrow band gap materials, which are commonly based on extended  $\pi$ -conjugated planar molecules<sup>16-18</sup> such as porphyrins and polycyclic aromatic hydrocarbons.<sup>11</sup> These structures are however especially vulnerable to solid state emission quenching due to the strong  $\pi$ - $\pi$  overlap favoring H-aggregation. As an alternative to extended  $\pi$ -conjugated systems, bathochromic tuning of emission color can also be realized through the introduction of strong donor (D) and acceptor (A) functionalities to the relatively short  $\pi$ -conjugated backbones in both intra- and/or inter-molecular manners.<sup>19-21</sup> A recently introduced A–D–A system by Shimizu et al. with cyano-substituents in the paraposition of the terminal rings and bis-diarlylamino functionalization in the central ring showed efficient DR/NIR emission (emission maximum  $\lambda_{em} = 702$  nm and florescence quantum yield  $\Phi_F = 0.33$  for powder) arising from an *intra*molecular charge-transfer (ICT) state,<sup>20</sup> where bulky side groups impede excessive excitonic (and

electronic) coupling. Novel solid state red emitters based on *inter*molecular CT states were recently designed and demonstrated by us which comprise a mixed stacked bi-chromophoric system ( $\lambda_{em} \sim 600$  nm and  $\Phi_F = 0.31$  for cocrystal form).<sup>19</sup>

Herein, we focus on a design of a DR/NIR emitting ICT-type solid state emitter, based on more complex, but synthetically facile D–A–D–A–D motif relying on the  $\beta$ -dicyanodistyrylbenzene (DCS) core.<sup>21</sup> Our design strategy provides DR/NIR emission arising from a strongly allowed electronic transition between balanced and delocalized frontier molecular orbitals (MOs). Avoiding bulky groups, but utilizing secondary interactions, the DCS moiety can smoothly adapt to external constraints by 'twist elasticity'<sup>19</sup> to give densely packed structure showing intense DR/NIR solid state emission.



Fig. 1 a) Molecular structure of  $\beta$ -MODEADCS. b) Normalized absorption and reflectance spectra (solid lines) and photoluminescence (dashed lines) spectra of solution (10  $\mu$ M in THF, black), pristine powder (red), and single crystal (blue) of  $\beta$ -MODEADCS.

Published on 15 October 2014. Downloaded by University of Prince Edward Island on 31/10/2014 07:12:38

**Table 1.** Photophysical properties of  $\beta$ -MODEADCS: fluorescence maxima ( $\lambda_{em}$ ), quantum yields ( $\Phi_F$ ), lifetimes ( $\tau_F$ ), radiative ( $k_r$ ) and non-radiative ( $k_{nr}$ ) decay rate.

	Solution <sup>[a]</sup>	powder	crystal <sup>[b]</sup>
$\lambda_{em}[nm]$	591	711	718
$\Phi_{\mathrm{F}}^{[\mathrm{c}]}$	0.88	0.42	0.36
$\tau_{\rm F}[\rm ns]$	2.3	6.9	7.1
$k_r / 10^7 [s^{-1}]^{[d]}$	38	6.1	5.1
$k_{nr}/10^7 [s^{-1}]^{[d]}$	5.2	8.5	9.0

[a]  $1 \times 10^{-5}$  M in tetrahydrofuran (THF). [b] Prepared by slow diffusion of methanol vapor into toluene solution. [c] Absolute quantum yield determined with a calibrated integrating sphere system. [d]  $k_r$  and  $k_{nr}$  were obtained by  $k_r = \Phi_F / \tau_F$ ,  $\tau_F - 1 = k_r + k_{nr}$ 



Fig. 2 (TD)DFT calculations of  $\beta$ -MODEADCS: a) frontier MO energies and topologies; b) optimized (gas phase) geometries of the ground and first excited state. c) Absorption and emission spectrum (pure electronic transition, Gaussian broadening; width 0.25 eV).

The molecular structure of novel  $\beta$ -dicyanodistyrylbenzene derivative, (2Z,2'Z)-3,3'-(2,5-dimethoxy-1,4-phenylene)bis(2-(4-diethylaminophenyl)acrylonitrile) ( $\beta$ -MODEADCS), is depicted in Fig. 1a.  $\beta$ -MODEADCS was synthesized by simple Knoevenagel reaction of 2-(4-diethylaminophenyl) acetonitrile with 2,5-dimethoxyterephthalaldehyde with a good yield. Details of the synthesis and characterization are described in the supporting information. High quality single crystals of  $\beta$ -MODEADCS were obtained by slow diffusion of methanol vapor into toluene solution.

β-MODEADCS exhibits intense red fluorescence in solution peaking at 591 nm (see Fig. 1b and Table 1). This corresponds to a bathochromic shift of 0.36 eV against the structurally related compound  $\beta$ -MODBDCS ( $\lambda_{em} = 505 \text{ nm}$ )<sup>21</sup> which carries a terminal alkoxy-group; this demonstrates the favourable donor strength of the terminal amino-group in β-MODEADCS to effectively tune the colour towards the DR/NIR region. Unlike the A-D-A system by Shimizu et al,<sup>20</sup> where the emission originated from an ICT state to result in a large apparent Stokes shift of more than 1.0 eV, β-MODEADCS shows an intense low energy absorption band at 486 nm, giving rise to a moderate Stokes shift of 0.45 eV. The experimental observations are confirmed by (time-dependent) density functional theory (TD)DFT calculations. According to the results shown in Fig. 2, the first excited singlet state  $(S_1)$  state is mainly formed by a promotion of an electron between the highest occupied and lowest unoccupied MOs (HOMO, LUMO), which show a largely delocalized character along the conjugated backbone. Concomitantly, in the present  $D\pi A\pi D\pi A\pi D$  system only minor ICT



**Fig. 3** Molecular stacking structures in single crystals of  $\beta$ -MODEADCS. a) ORTEP representation (50% probability ellipsoids) from top (top) and side (bottom) view. H atoms are omitted for clarity. b) Unit cell representation (space group =  $P_{\overline{1}}$ , Z = 1, a = 4.71 Å, b = 9.30 Å, c = 16.85 Å,  $\alpha$  = 100.1°,  $\beta$  = 92.6°,  $\gamma$  = 99.4°). c) Top view and illustration of intermolecular interactions. d) Side view and pitch angle.

character is observed, and the oscillator strength is thus large for ground to S<sub>1</sub> state transition ( $f_{S1} = 1.61$ ). This is very different from the common A- $\pi$ -D- $\pi$ -A motif with pronounced ICT character and small oscillator strength ( $f_{S1} = 0.115$  for 1a, ref 20); for details see supporting information. The large oscillator strength in  $\beta$ -MODEADCS gives rise to a large radiative rate k<sub>r</sub> (Table 1), which easily competes with the non-radiative rate k<sub>nr</sub> to exhibit very strong fluorescence with a quantum yield of  $\Phi_F = 0.88$ . The unstructured absorption and emission spectra are attributed to strongly twisted equilibrium structures in the S<sub>0</sub> and S<sub>1</sub> states respectively,<sup>22</sup> as indeed confirmed by the (TD)DFT calculations (Fig. 2).

Single crystals of  $\beta$ -MODEADCS show DR/NIR emission peaking at 718 nm, thus bathochromically shifted by ca. 0.4 eV compared to solution; see Fig. 1. The fluorescence quantum yield of 0.36 is noted to be very high for DR/NIR solid state emitters; for powder samples  $\Phi_F = 0.42$  was observed, due to further reduced reabsorption,<sup>23</sup> The fluorescence lifetime ( $\tau_F$ ) of the crystal is 7.1 ns, which thus gives a radiative rate  $(k_r)$  of  $5.1 \times 10^7$  s<sup>-1</sup>. This is about a factor of eight lower than in solution, giving direct evidence for (weak) H-aggregation, as recently reviewed.<sup>8</sup> From the reflectance spectra in Fig. 1, H-aggregation is difficult to confirm, because of the broad plateaus ranging from about 470 nm to 600 nm which are due to the high optical density of the solid state samples.<sup>7</sup> The onset of absorption (ca. 710 nm) is similarly red-shifted against solution as the emission band. Solid-state spectral shifts in emitting conjugated organic materials are commonly ascribed to a combined effect of excitonic coupling and the (anisotropic) polarizability in the solid state compared to solution.<sup>7</sup> These shifts are however usually not larger than 0.3 eV,<sup>7,24</sup> while additional excimeric effects can significantly enlarge the solid-state shifts.<sup>7,21,25</sup> Excimeric effects arise from partial intermolecular CT character of the responsible electronic transition and give rise to broad, vibronically unresolved emission features,<sup>25</sup> just as it is seen for  $\beta$ -MODEADCS

To gain full insight into the solid-state emission behavior of  $\beta$ -MODEADCS, the molecular stacking was comprehensively evaluated through X-ray structural investigations. According to the X-ray single crystal analysis,  $\beta$ -MODEADCS crystallizes in the triclinic space group  $P_{\overline{1}}$  with one molecule per unit cell, as shown in Fig. 3. Dense packing of the molecules with well-defined secondary bonding motifs force the molecule into a planar geometry (Fig. 3c) as recently reviewed,<sup>8,26</sup> while in solution the ground state is expected to be largely non-planar as predicted from the DFT calculations (Fig. 2). Adjacent molecules are arranged in a quasi

Published on 15 October 2014. Downloaded by University of Prince Edward Island on 31/10/2014 07:12:38

Journal Name

one-dimensional slipped  $\pi$ -stack with an inter-plane distance of 3.57 Å, a pitch angle of 47° (Fig. 3d), and a roll angle of 76°. The arrangement indeed points to weak H-aggregation, and at the same time should allow for sufficient  $\pi - \pi$  overlap for intermolecular charge transfer as suggested from the photophysical analysis. For further confirmation, we performed TD-DFT calculations for monomer and dimer (see supporting information for calculational details). Natural transition orbital (NTO) analysis for the two species confirm moderate H-aggregation with a forbidden S<sub>1</sub> state ( $f_{S1} =$ 0.00) and an excitonic splitting of 0.29 eV (see Fig. S6), which represent the main excitonic interaction in the crystal.

The powder X-ray diffraction (PXRD) patterns of the solid samples (see Fig. S7, supporting information) corresponds well with those of the single crystal and the simulated PXRD pattern calculated from the single crystal X-ray data, suggesting that the packing structures of powder and single crystal samples are identical. We noted above that the powder samples of  $\beta$ -MODEADCS showed the same bright DR/NIR emission properties as the single crystal with essentially the same photophysics (Table 1). This is especially remarkable since H-type polycrystalline samples are usually vulnerable to trapping, so that the high quantum yield found in the single crystals are strongly reduced in powders, films or nanoparticles.<sup>7</sup> In  $\beta$ -MODEADCS, trapping in the powder sample might be reduced by low exciton diffusion due to the moderate coupling, as well as the strong secondary interactions which prohibit structural trapping.<sup>8,27</sup>

In summary, we have synthesized  $\beta$ -MODEADCS as a novel solid state DR/NIR emitter ( $\lambda_{em} = 711$  nm) with a high quantum yield of 42 %. The emission properties were fully rationalized in a combined structural, spectroscopic and quantum-chemical analysis. The narrow band gap and the intense DR/NIR emission color of  $\beta$ -MODEADCS arises from the D–A–D–A–D motif with strong donor and acceptor functionalities and at the same time largely delocalized frontier MOs, giving rise to a large oscillator strength of the emitting state. In the crystal,  $\beta$ -MODEADCS forms weak H-aggregates of a slipped  $\pi$ -stacked arrangement aided by secondary interactions, resulting in high fluorescence quantum yields of powder samples and single crystals. The D–A–D–A–D motif thus commends itself as a viable strategy to effectively achieve bright solid-state DR/NIR emitters, avoiding extended  $\pi$ -conjugated systems.

This work was supported by the National Research Foundation of Korea (NRF) through a grant funded by the Korean Government (MSIP; No. 2009-0081571). The work at IMDEA was supported by the Spanish Ministerio de Economía y Competitividad (MINECO; project CTQ2011-27317), by the Comunidad de Madrid (Projects S2009/MAT-1726, S2009/PPQ-1533) and by the Campus of International Excellence (CEI) UAM+CSIC.

#### Notes and references

<sup>*a*</sup> Center for Supramolecular Optoelectronic Materials and WCU Hybrid Materials Program, Department of Materials Science and Engineering, Seoul National University, ENG 445, Seoul 151-744, Korea.

<sup>b</sup> Madrid Institute for Advanced Studies, IMDEA Nanoscience, C/ Faraday 9, Campus Cantoblanco, 28049 Madrid, Spain.

 $\dagger$  Electronic Supplementary Information (ESI) available: experimental details for synthesis and characterization of β-MODEADCS. Single crystal and powder X-ray diffraction data, fluorescence decay kinetics, and computational results. See DOI: 10.1039/c000000x/

- 1 K. Müllen and U. Scherf, Organic Light Emitting Devices: Senthesis, Properties ans Applications; Wiley-VCH: 2006.
- 2 G. M. Farinola, R. Ragni, Chem. Soc. Rev., 2011, 40, 3467.
- 3 I. D. W. Samuel and G. A. Turnbull, Chem. Rev., 2007, 107, 1272.

- 4 L. Basabe-Desmonts, D. N. Reinhoudt, and M. Crego-Calama, *Chem. Soc. Rev.*, 2007, 36, 993.
- 5 A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher, and T. E. Rice, *Chem. Rev.*, 1997, **97**, 1515.
- 6 R. Weissleder and M. J. Pittet, *Nature*, 2008, 452, 580.
- 7 J. Gierschner, L. Luer, B. Milian-Medina, D. Oelkrug, and H. J. Egelhaaf, J. Phys. Chem. Lett., 2013, 4, 2686.
- J. Gierschner and S. Y. Park, *J. Mater. Chem. C*, 2013, 1, 5818.
   S. Y. Chen, X. J. Xu, Y. Q. Liu, G. Yu, X. B. Sun, W. F. Qiu, Y. Q. Ma and D. D. Zhu, *Als. Funct. Matur.* 2005, 15, 1541.
- Ma, and D. B. Zhu, *Adv. Funct. Mater.*, 2005, **15**, 1541.
  H. Y. Li, Z. G. Chi, X. Q. Zhang, B. J. Xu, S. W. Liu, Y. Zhang, and J. R. Xu, *Chem. Commun.*, 2011, **47**, 11273.
- 11 M.-J. Lin, A. J. Jimenez, C. Burschka, and F. Wurthner, *Chem. Commun.*, 2012, 48, 12050.
- 12 C. H. Zhao, Y. H. Zhao, H. Pan, and G. L. Fu, *Chem. Commun.* 2011, 47, 5518.
- 13 B. K. An, S. K. Kwon, S. D. Jung, and S. Y. Park, J. Am. Chem. Soc., 2002, 124, 14410.
- 14 T. E. Kaiser, H. Wang, V. Stepanenko, and F. Wurthner, *Angew. Chem. Int. Ed.*, 2007, **46**, 5541.
- 15 Z. Q. Xie, B. Yang, F. Li, G. Cheng, L. L. Liu, G. D. Yang, H. Xu, H. L. Ye, M. Hanif, S. Y. Liu, D. G. Ma, and Y. G. Ma, *J. Am. Chem. Soc.*, 2005, **127**, 14152.
- 16 C. Y. Du, S. H. Ye, Y. Q. Liu, Y. L. Guo, T. Wu, H. T. Liu, J. A. Zheng, C. Cheng, M. L. Zhu, and G. Yu, *Chem. Commun.*, 2010, 46, 8573.
- 17 B. B. Jang, S. H. Lee, and Z. H. Kafafi, Chem. Mater., 2006, 18, 449.
- 18 M. A. Wolak, J. Delcamp, C. A. Landis, P. A. Lane, J. Anthony, and Z. Kafafi, *Adv. Funct. Mater.*, 2006, 16, 1943.
- 19 S. K. Park, S. Varghese, J. H. Kim, S. J. Yoon, O. K. Kwon, B. K. An, J. Gierschner, and S. Y. Park, S. Y. J. Am. Chem. Soc., 2013, 135, 4757.
- 20 M. Shimizu, R. Kaki, Y. Takeda, T. Hiyama, N. Nagai, H. Yamagishi, and H. Furutani, *Angew. Chem. Int. Ed.*, 2012, **51**, 4095.
- 21 S. J. Yoon, S. Varghese, S. K. Park, R. Wannemacher, J. Gierschner, and S. Y. Park, Adv. Opt. Mater., 2013, 1, 232.
- 22 B. Milian-Medina, S. Varghese, R. Ragni, H. Boerner, E. Orti, G. M. Farinola, and J. Gierschner, J. Chem. Phys., 2011, 135, 124509.
- 23 For the fluorescence measurements of the single crystals much effort was done to minimize reabsorption, selecting particularly small crystals. To record the emission spectra and lifetimes, the light was focused to the very edge of the crystal.
- 24 J. Gierschner, J. Cornil, and H. J. Egelhaaf, Adv. Mater., 2007, 19, 173.
- 25 J. Gierschner, M. Ehni, H. J. Egelhaaf, B. Milian Medina, D. Beljonne, H. Benmansour, and G. C. Bazan, J. Chem. Phys., 2005, 123, 144914.
- 26 B. K. An, J. Gierschner, and S. Y. Park, Acc. Chem. Res., 2012, 45, 544.
- 27 (Structural) trapping is indeed a sensitive function of the intermolecular arrangement. Concomitantly, in other polymorphs of  $\beta$ -MODEADCS, which can be realized e.g. by fast precipitation from solvent mixtures, fluorescence quantum yields are significantly lower (see supporting information).

TOC contents for:

## A Distyrylbenzene Based Highly Efficient Deep Red/Near-Infrared Emitting Organic Solid

A highly efficient deep red/near-infrared emitting organic solid based on β-dicyanostyrylbenzene derivative was reported.

