

CHEMISTRY A European Journal



Accepted Article

Title: Red-emitting Delayed Fluorescence and Room Temperature Phosphorescence from Core-substituted Naphthalene Diimides

Authors: Suman Kuila, Anaranya Ghorai, Pralok K. Samanta, Raja B. K. Siram, Swapan K. Pati, K. S. Narayan, and Subi J. George

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: Chem. Eur. J. 10.1002/chem.201904651

Link to VoR: http://dx.doi.org/10.1002/chem.201904651

Supported by ACES



COMMUNICATION

WILEY-VCH

Red-emitting Delayed Fluorescence and Room Temperature Phosphorescence from Core-substituted Naphthalene Diimides

Suman Kuila,^[a] Anaranya Ghorai,^[b] Pralok K. Samanta,^[c] Raja B. K. Siram,^[a] Swapan K. Pati,^[c] K. S. Narayan^[b] and Subi J. George*^[a]

Dedicated to Professor C. N. R. Rao on the occasion of his 85th birthday

Abstract: Unprecedented ambient triplet mediated emission in coresubstituted naphthalene diimide (cNDI) derivatives is unveiled via delayed fluorescence and room temperature phosphorescence. Carbazole core-substituted cNDIs, with a donor-acceptor design, showed deep-red triplet emission in solution processable films with high quantum yield. This study, with detailed theoretical calculations and time-resolved emission experiments, enables new design insights into the triplet harvesting of cNDIs; an important family of molecules which has been, otherwise, extensively investigated for its n-type electronic character and tunable singlet fluorescence.

1,4,5,8-Naphthalenetetracarboxylic acid diimides (NDIs) are a very important class of molecules in functional organic and supramolecular materials.^[1] NDIs have been extensively used in organic FETs and photovoltaic applications as air-stable, n-type semiconductors.^[2] Improved synthetic methodologies to access library of core-substituted NDIs (cNDIs) with tunable energetic levels have further expanded its scope to various optoelectronic and sensor applications and also as a model system in supramolecular chemistry.^[1a,3] Novel anion- π interactions have been experimentally realized in electron deficient cNDIs and later used in halide sensing, organocatalysis and for anion transport through lipid bilayers.^[4-6] Remarkably, air-stable radical anions of cNDI derivatives are now synthetically feasible^[7] and may be of potential use in artificial photosynthetic cascades for efficient solar energy conversion.^[8] Apart from its electronic properties, the tunable fluorescence of cNDIs in solution are used in energy transfer and circularly polarized luminescence.^[9] However, for advanced luminescence applications such as solid state lighting and organic light emitting diodes (OLEDs), triplet harvesting of these molecules is an important requirement to improve the efficiency of these devices.[10]

[a]	S. Kuila, Dr. R. B. K. Siram, Prof. Dr. S. J. George
	New Chemistry Unit and School of Advanced Materials (SAMat)
	Jawaharlal Nehru Centre for Advanced Scientific Research
	(JNCASR) Jakkur, Bangalore 560064, India
	E-mail: george@incasr.ac.in, subijg@gmail.com
[b]	A. Ghorai, Prof. Dr. K. S. Naravan

- Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR)
- [c] Dr. P. K. Samanta, Prof. Dr. S. K. Pati Theoretical Science Unit, Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR)

Supporting information for this article is given via a link at the end of the document.



Figure 1. a) Molecular structures and corresponding sample photographs of **CzNDI** (left) and **CzPhNDI** (right). b) Natural transition orbitals for S₁ state at the optimized S₀ geometry for optical absorption of **CzNDI** (left) and **CzPhNDI** (right) calculated using 0[°]B97XD/6-31+g(d) level of theory in vacuum. Hole and electron wave functions with the largest weight (*v*) and the oscillator strength for the transition (f) are also provided. c) Proposed singlet and triplet energy states of **CzNDI** (left) and **CzPhNDI** (right). F = fluorescence, DF = delayed fluorescence, P = phosphorescence.

In this respect, however, NDIs are relatively unexplored in spite of the presence of multiple carbonyl groups in its core to promote fast intersystem crossing (ISC) and despite having excellent triplet yield. [11] Very recently, efforts have been made in stabilizing these NDI triplets by heavy atom substitution or by intermolecular charge-transfer in confined supramolecular microenvironments, to harvest ambient room temperature phosphorescence (RTP).^[12] However, molecular engineering of cNDIs to modulate the excited state energy levels (Sn and Tn) and emission wavelengths and also to realize other means of triplet harvesting such as thermally activated delayed fluorescence and triplet-triplet annihilation up-conversion still remains a challenge. We envisage that low lying triplets of cNDIs would also benefit in the design of red to NIR triplet emitters.^[13] Charge-transfer (CT) states created by the spatially separated donor and acceptor subunits is a crucial design to obtain a small singlet-triplet gap (ΔE_{ST}) to aid triplet mediated delayed emission from chromophores.^[10a,14] In this work, we introduce a donor-acceptor molecular design to harvest the triplets in cNDI derivatives, by

COMMUNICATION



Figure 2. a) Synthetic scheme for **CzNDI** and **CzPhNDI**. Reagents and conditions: i) 1,1-dibromo-5,5-dimethylhydantoin, conc. H₂SO₄, 50 °C, 24 h, 93%; ii) n-octyl amine, acetic acid, 100 °C, 24 h, 88%; iii) Carbazole, Pd(OAc)₂, P(o-tol)₃ potassium *tert*-butoxide, toluene, 120 °C, 24 h, 42%; iv) 9H-Carbazole-9-(4-phenyl)boronic acid pinacol ester, Pd(PPh₃)₄, aq. K₂CO₃, toluene, 120 °C, 24 h, 64%. b) Absorption and normalized emission spectra of **CzNDI** and **CzPhNDI** in THF (**[CzNDI**] and **[CzPhNDI**] = 0.05 mM, $\lambda_{exc.}$ = 380 nm) and c) corresponding lifetime decay spectra collected at the locally excited emission wavelength (430 nm) and charge-transfer emission wavelength (580 nm). IRF is the instrument response function and $\lambda_{exc.}$ = 373 nm; d) Natural transition orbitals for S₁ states at optimized S₁ state geometry for emission of **CzNDI** (left) and **CzPhNDI** (right) using B97XD/6-31+g(d) level of theory in vacuum. Hole and electron wave functions with the largest weight (v), the oscillator strength for the transitions (f) are also provided.

substituting the electron-deficient NDI cores with carbazole (Cz) donor moieties. Remarkably, these core-substituted NDI derivatives **CzNDI** and **CzPhNDI**, showed red-emitting delayed fluorescence (DF) and room temperature phosphorescence (RTP), phenomena rarely reported in NDI based molecules (Figure 1a). With detailed time dependent density functional theory (TDDFT) calculations and time-resolved emission spectroscopy, further we provide a structure-property study on how to increase the oscillator strength of emission in these cNDI derivatives, which depends heavily on the excited state geometry of the chromophores.

CzNDI and CzPhNDI were synthesized from dibromo naphthalene diimide derivative 3, using Pd-catalysed Buchwald-Hartwig amination and Suzuki coupling reactions, respectively (Figure 2a, Supporting Information), TDDFT studies of the ground state geometries (S₀) revealed dihedral angles of 57° and 61° between donor (Cz) and acceptor (NDI) moieties for CzPhNDI and CzNDI, respectively (Table S1). Further natural transition orbital (NTO) analysis was performed to understand the nature of transitions in the molecules. In both molecules for optical absorption to S₁ state, the hole NTO is localized on carbazole units and the electron NTO is localized on NDI core, in consistent with the molecular design having suitable charge-transfer transitions (Figure 1b). This was further supported experimentally by cyclic voltametry (CV) studies where highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbital energies were estimated (Figure S1). The calculated HOMO energies of CzNDI and CzPhNDI were -5.26 eV and -5.17 eV, respectively. The calculated LUMO energies of CzNDI and CzPhNDI were -3.86 eV and -3.71 eV respectively. The HOMO and LUMO energy levels closely match with the HOMO level of carbazole and NDI LUMO levels, respectively.^[15] This observation also shows the spatial separation of HOMO-LUMO for a suitable charge-transfer state formation in the molecules in their ground states.^[13c]

In solution state (THF), both CzNDI and CzPhNDI show a locally excited (LE) absorption band at around 300-400 nm and a charge-transfer (CT) band in the longer wavelengths (420-650 nm) (Figure 2b). The locally excited or charge-transfer nature of the absorption bands were confirmed by their sensitivity towards the polarity of the solvents (Figure S2). Both the molecules showed characteristic LE emission bands with sharp vibrational features at 400-500 nm with short lifetime (0.99 ns and 0.90 ns for CzNDI and CzPhNDI, respectively) on excitation at 380 nm (Figures 2b-c). Interestingly, CzPhNDI showed a CT emission with a maximum at 580 nm, whereas CzNDI does not show any CT emission in THF (λ_{exc} = 380 nm, Figure 2b and Figure S2). The CT nature of CzPhNDI emission is evident from the long lifetime of 9.3 ns and its solvatochromic behaviour ($\lambda_{exc} = 373$ nm. $\lambda_{\text{monitored}}$ = 580 nm) (Figure 2c and Figure S2). In order to get further insight into this remarkable difference in emission characteristics, we theoretically investigated the nature of excited states using TDDFT methods. In the excited state of CzNDI, the Cz and NDI units are found to be perpendicular to each other (dihedral angle ~90°), thus forming a stable twisted intramolecular charge transfer (TICT) state (S₁), with complete spatial separation of hole and electron wavefunctions (Figure 2d, left panel); a geometry that weakens the transition dipole moment matrix element as evident from the low oscillator strength of emission (f = 0.00). On the contrary, due to the presence of a phenyl spacer in CzPhNDI, the TICT state is not stable and both the Cz and NDI units tend to adapt a more planar conformation (dihedral angle $\sim 2^{\circ}$) in its optimized excited (S₁) state (Table S1-S2). This leads to a comparatively higher spatial overlap between hole and

COMMUNICATION



Figure 3. a) Normalized emission spectra of the PMMA films of **CzPhNDI** at different temperature with varying delay times (0.5 ms and 20 ms) showing DF and phosphorescence. Temperature dependent lifetime decay profiles of **CzPhNDI** monitored at b) 640 nm and c) 550 nm. d) Comparision of steady-state emission intensity of **CzPhNDI** in air and under vacuum and the inset shows the photograph of **CzPhNDI** film under 365 nm UV-lamp. e) Normalized emission spectra of PMMA films of **CzNDI** at different temperatures with different delay times (50 μs and 20 ms) showing DF and phosphorescence. Inset: Photograph of **CzNDI** in film state under 365 nm UV-lamp. f) Lifetime decay spectra of **CzNDI** at different temperatures (λ_{monitored} = 680 nm). In all cases 1 wt. % **CzNDI** or **CzPhNDI** in PMMA was used and the excitation wavelength was 380 nm.

electron wavefunctions with large oscillator strength (f = 0.40) for S_1 - S_0 transition leading to emissive CT for **CzPhNDI** (Figure 2d, right panel, Table S1-S2). Thus it is evident that a balance between twist angle and HOMO-LUMO overlap is crucial for high photoluminescence quantum yield in cNDI derivatives.

In an attempt to harvest the triplets in these cNDI derivatives, we further studied them in solid state as non-radiative pathways arising from vibrational relaxation can quench the triplet excitons in solution state. However, neat thin films of both CzNDI and CzPhNDI, made from chloroform solutions showed only weak emission due to the aggregation induced quenching (Figure S3-S4). On the other hand, emission spectra of CzNDI and CzPhNDI dispersed in poly(methylmethacrylate) (PMMA, 1 wt. % dye to polymer ratio, $\lambda_{exc.}$ = 380 nm) showed a substantial blue-shift (30 nm and 50 nm for CzNDI and CzPhNDI, respectively) and concomitant enhancement in charge-transfer (CT) emission intensity compared to neat films (Figure S3-S4) suggesting less aggregation and also a plausible triplet state stabilization due to reduced oxygen diffusion contributing effectively in the total emission (vide infra).^[16] Unlike the solution state, the intensity of LE emission (400-500 nm) in PMMA films was less compared to the CT emission and hence all further studies were focussed on CT emission. CzPhNDI films showed higher emission quantum yield of 32% compared to the 2% of CzNDI.

To elucidate the triplet contribution in the emission of **CzPhNDI** detailed time-resolved and temperature dependent fluorescence spectroscopy measurements were performed by exciting the LE state at 380 nm. Steady-state emission at 300 K, showed a broad emission (500-800 nm) with a maximum at 640 nm (Figure 3a). Interestingly, a gated emission spectrum with a short time delay (0.5 ms) showed similar emission spectrum

suggesting the presence of a delayed emission in CzPhNDI chromophores (Figure 3a). Further, the gated emission with a longer delay time of 20 ms at 300 K, revealed vibronic features in the 600-800 nm range, accompanied by a broad structureless emission band at 550-600 nm with reduced intensity, hinting towards the presence of an additional low energy excited state. Low temperature (15 K) gated emission (20 ms delay) further showed that the emission band in the 600-800 nm region retains its vibronic spectral features with the complete disappearance of the emission contribution in the 550-600 nm suggesting its phosphorescence nature. This was further confirmed by temperature dependent, time-resolved emission measurements at different temperatures ($\lambda_{monitored}$ = 640 nm), which showed a decrease in average lifetime on increasing temperature (tavg. = 6.45 ms and 2.43 ms at 15 K and 300 K, respectively, Figure 3b).^[17] Along with this long lifetime decay, CzPhNDI also showed a prompt CT fluorescence with an average lifetime of 7.3 ns ($\lambda_{exc.}$ = 373 nm, $\lambda_{\text{monitored}}$ = 640 nm) (Figure S5). On the other hand, average lifetime of the delayed emission at lower wavelength region, selectively monitored at 550 nm showed an increase in lifetime with increase in temperature ($\lambda_{exc.}$ = 380 nm, t_{avg.} = 78 µs and 1.2 ms at 15 K and 300 K, respectively) characteristic of molecules with delayed fluorescence (DF) mediated via triplet excitons (Figure 3c) consistent with its small singlet-triplet energy gap ($\Delta E_{ST} = 0.17 \pm 0.03 \text{ eV}$). In addition, a threefold increase in emission intensity and corresponding increase in average lifetime under vacuum compared to the emission under ambient conditions, reiterates the contribution from triplet states in CzPhNDI emission (Figure 3d, Figure S6).^[13c] Low temperature solvatochromism studies with appropriate control molecules further revealed that triplet states are of locally excited character

COMMUNICATION

originating from the acceptor NDI unit rather than charge-transfer in nature (Figure S7-S9). These experiments provides an unequivocal proof for the co-existence of both DF and RTP emission in the red-wavelength region with excellent quantum yield. To the best of our knowledge, this is the first report of dual DF and RTP from donor-acceptor cNDI derivatives under ambient conditions.^[12] Direct excitation at the charge-transfer band at 500 nm, also resulted in similar spectroscopic features suggesting that triplet state harvesting is possible via both LE and CT states (Figure S10).

On the other hand, PMMA (1 wt. %) films of CzNDI showed a weak CT emission ($\lambda_{exc.}$ = 380 nm) in the 550-800 nm region unlike its non-fluorescent nature in solution state (Figure 3e) with a prompt lifetime of 3.45 ns ($\lambda_{exc.}$ = 373 nm, $\lambda_{monitored}$ = 680 nm), probably due to a non-orthogonal, excited state conformation in the solid-state (Figure S11). Delayed emission feature is also observed for CzNDI films at 300 K as confirmed by a gated emission spectrum (delay time = 50 μ s, $\lambda_{exc.}$ = 380 nm) in the same wavelength region (550-800 nm, λ_{max} = 680 nm) hinting towards similar DF and RTP characteristics like CzPhNDI (Figure 3a and 3e). Time-gated emission spectra (20 ms delay time, λ_{exc} , = 380 nm) obtained at 15 K showed a 80 nm red-shift compared to room temperature steady-state emission (Figure 3e). This low energy emission with a maximum at 680 nm, can be attributed to the locally excited phosphorescence because of its high lifetime (tavg.= 3.1 ms, $\lambda_{\text{exc.}}$ = 380 nm, $\lambda_{\text{monitored}}$ = 680 nm) (Figure 3f, Figure S12a). However, unlike CzPhNDI, this phosphorescence band neither originates from carbazole (donor) or NDI (acceptor) components (Figure S12b). Similar phosphorescence behaviour

Acknowledgements

Funding from Technology Research Centre at JNCASR (JNC/DST/TRC/SJG-KSN/4397) & DST-JNCASR Nanomission Project (SR/NM/TP-25/2016) by Government of India are greatly acknowledged. S. K. thanks UGC; A. G. and P. K. S. thank JNCASR for fellowship. The authors thank Prof. Satish Patil, SSCU, IISc for fruitful discussions.

Keywords: Donor-acceptor systems• Naphthalenediimide• Delayed Fluorescence• Room Temperature Phosphorescence • Charge-transfer.

- a) N. Sakai, J. Mareda, E. Vauthey, S. Matile, *Chem. Commun.* 2010, 46, 4225-4237; b) S. V. Bhosale, C. H. Jani, S. J. Langford, *Chem. Soc. Rev.* 2008, *37*, 331-342.
- a) J. H. Oh, S.-L. Suraru, W.-Y. Lee, M. Könemann, H. W. Höffken, C. Röger, R. Schmidt, Y. Chung, W.-C. Chen, F. Würthner, Z. Bao, *Adv. Funct. Mater.* 2010, *20*, 2148-2156; b) T. He, M. Stolte, F. Würthner *Adv. Mater.* 2013, *25*, 6951-6955; c) H. Yan, Z. Chen, Y. Zheng, C. Newman, J. R. Quinn, F. Dötz, M. Kastler, A. Facchetti, *Nature* 2009, *457*, 679-686.
- [3] a) S.-L. Suraru, F. Würthner, Angew. Chem. Int. Ed. 2014, 53, 7428-7448; b) F. Würthner, S. Ahmed, C. Thalacker, T. Debaerdemaeker, Chem. Eur. J. 2002, 8, 4742-4750; b) C. Röger, F. Würthner, J. Org. Chem. 2007, 72, 8070-8075; c) R. S. K. Kishore, V. Ravikumar, G. Bernardinelli, N. Sakai, S. Matile, J. Org. Chem. 2008, 73, 738-740; d) A. Takai, T. Yasuda, T. Ishizuka, T. Kojima, M. Takeuchi, Angew. Chem. Int. Ed. 2013, 52, 9167-9171.
- [4] a) S. Guha, S. Saha, J. Am. Chem. Soc. 2010, 132, 17674-17677; b) S.
 Guha, F. S. Goodson, L. J. Corson, S. Saha, J. Am. Chem. Soc. 2012, 134, 13679-13691.

at low temperatures has been recently shown in donor-acceptor cNDI derivatives, wherein certain conformations of the molecule lead to enhanced conjugation between the donor (triphenyl amine) and acceptor sub-units (NDI) resulting in new locally excited triplet state.^[13b] In addition, gradual decrease in the lifetime on increasing the temperature (Figure 3f) reiterates (3.1 ms at 15 K to 80.5 μ s at 300 K, λ_{exc} = 380 nm, $\lambda_{monitored}$ = 680 nm) its phosphorescence character similar to CzPhNDI at this wavelength. Accordingly, temperature dependent steady-state emission also showed a gradual red-shift (652 nm to 672 nm) and enhanced emission intensity on decreasing the temperature (Figure S13). Presence of triplet mediated ($\Delta E_{ST} = 0.15 \pm 0.02 \text{ eV}$) deep-red-NIR dual DF and RTP emission was further confirmed via various experiments (Figure S14-S16). However, overall quantum yield (2 %) was found to be much weaker than CzPhNDI.

In conclusion, we have shown an efficient dual DF and RTP emission under ambient and amorphous conditions from cNDI derivatives by a clever molecular design to facilitate the triplet harvesting. Time-resolved photoluminescence studies and TDDFT calculations further provided a structure-property relationship to fine-tune the emission oscillator strength and charge-transfer states of these donor-acceptor molecules. We envisage that this study opens up an exciting, hitherto unexplored triplet harvesting of interesting class of cNDI family, by using the well-established, rich chemistry of core-substitution. Further extension of these designs to other electron deficient arylene diimides would be the next step to achieve NIR-emitting tripletemitting dyes for applications in bio-imaging and OLEDs.^[18]

- a) Y. Zhao, Y. Domoto, E. Orentas, C. Beuchat, D. Emery, J. Mareda, N. Sakai, S. Matile, *Angew. Chem. Int. Ed.* 2013, *52*, 9940-9943; b) L. Liu, Y. Cotelle, A.-B. Bornhof, C. Besnard, N. Sakai, S. Matile, *Angew. Chem. Int. Ed.* 2017, *56*, 13066-13069.
- [6] R. E. Dawson, A. Hennig, D. P. Weimann, D. Emery, V. Ravikumar, J. Montenegro, T. Takeuchi, S. Gabutti, M. Mayor, J. Mareda, C. A. Schalley, S. Matile, *Nat. Chem.* **2010**, *2*, 533-538.
- [7] a) Y. Kumar, S. Kumar, K. Mandal, P. Mukhopadhyay, Angew. Chem. Int. Ed. 2018, 57, 16318-16322; b) S. Kumar, M. R. Ajayakumar, G. Hundal, P. Mukhopadhyay, J. Am. Chem. Soc. 2014, 136, 12004-12010; c) G. Bélanger-Chabot, A. Ali, F. P. Gabbaï, Angew. Chem. Int. Ed. 2017, 56, 9958-9961.
- [8] P. D. Frischmann, K. Mahata, F. Würthner, Chem. Soc. Rev. 2013, 42, 1847-1870.
- [9] a) A. Sarkar, S. Dhiman, A. Chalishazar, S. J. George, Angew. Chem. Int. Ed. 2017, 56, 13767-13771; b) R. Sethy, J. Kumar, R. Métivier, M. Louis, K. Nakatani, N. Mohan, T. Mecheri, A. Subhakumari, K. G. Thomas, T. Kawai, T. Nakashima, Angew. Chem. Int. Ed. 2017, 56, 15053-15056; c) A. Takai, M. Takeuchi, Bull. Chem. Soc. Jpn. 2018, 91, 44–51.
- [10] a) H. Uoyama, K. Goushi, K. Shizu, H. Nomura, C. Adachi, *Nature* 2012, 492, 234-238; b) M. Y. Wong, E. Zysman-Colman, *Adv. Mater.* 2017, 29, 1605444.
- a) P. Ganesan, J. Baggerman, H. Zhang, E. J. R. Sudhölter, H. Zuilhof, J. Phys. Chem. A 2007, 111, 6151-6156; b) O. Yushchenko, G. Licari, S. Mosquera-Vazquez, N. Sakai, S. Matile, E. Vauthey, J. Phys. Chem. Lett. 2015, 6, 2096-2100.
- [12] a) S. Kuila, K. V. Rao, S. Garain, P. K. Samanta, S. Das, S. K. Pati, M. Eswaramoorthy, S. J. George, *Angew. Chem. Int. Ed.* 2018, *57*, 17115-17119; b) V. Martinez-Martinez, R. S. Llano, S. Furukawa, Y. Takashima, I. L. Arbeloa, S. Kitagawa, *ChemPhysChem* 2014, *15*, 2517-2521.
- [13] a) J. H. Kim, J. H. Yun, J. Y. Lee, *Adv. Opt. Mater.* 2018, *6*, 1800255; b)
 H. F. Higginbotham, P. Pander, R. Rybakiewicz, M. K. Etherington, S. Maniam, M. Zagorska, A. Pron, A. P. Monkman, P. Data, *J. Mater. Chem. C* 2018, *6*, 8219-8225; c) F. B. Dias, J. Santos, D. R. Graves, P. Data,

COMMUNICATION

R. S. Nobuyasu, M. A. Fox, A. S. Batsanov, T. Palmeira, M. N. Berberan-Santos, M. R. Bryce, A. P. Monkman, *Adv. Sci.* **2016**, *3*, 1600080.

- [14] a) Y. Tao, K. Yuan, T. Chen, P. Xu, H. Li, R. Chen, C. Zheng, L. Zhang, W. Huang, *Adv. Mater.* 2014, *26*, 7931-7958; b) Y. Im, M. Kim, Y. J. Cho, J.-A Seo, K. S. Yook, J. Y. Lee, *Chem. Mater.* 2017, *29*, 1946-1963; c) T. J. Penfold, F. B. Dias, A. P. Monkman, *Chem. Commun.* 2018, *54*, 3926-3935.
- [15] J. Shukla, M. R. Ajayakumar, P. Mukhopadhyay, Org. Lett. 2018, 20, 7864-7868. Attempt has been made towards synthesizing similar derivative; however triplets are not explored in this work.
- [16] D. Lee, O. Bolton, B. C. Kim, J. H. Youk, S. Takayama, J. Kim, J. Am. Chem. Soc. 2013, 135, 6325-6329.
- [17] L. Yu, Z. Wu, C. Zhong, G. Xie, Z. Zhu, D. Ma, C. Yang, Adv. Opt. Mater. 2017, 5, 1700588.
- [18] a) M. Schulze, A. Steffen, F. Würthner, *Angew. Chem. Int. Ed.* 2015, *54*, 1570-1573; b) X. Zhen, Y. Tao, Z. An, P. Chen, C. Xu, R. Chen, W. Huang, K. Pu, *Adv. Mater.* 2017, *29*, 1606665; c) N. Gan, H. Shi, Z. An, W. Huang, *Adv. Funct. Mater.* 2018, *28*, 1802657.

COMMUNICATION

COMMUNICATION



Air-stable, amorphous and purely organic triplet mediated red emission is achieved via delayed fluorescence and room temperature phosphorescence from donor (carbazole) core-substituted, naphthalene diimide molecules.

Suman Kuila, Anaranya Ghorai, Pralok K. Samanta, Raja Bhaskar Kanth Siram, Swapan K. Pati, K. S. Narayan, and Subi J. George*

Page No. – Page No.

Red-emitting Delayed Fluorescence and Room Temperature Phosphorescence from Core-Substituted Naphthalene Diimides