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journal homepage: www.elsevier.com/locate/dyepig

Highly fluorescent blue-green emitting phenanthroimidazole derivatives: Detail experimental and DFT study of structural and donating group effects on fluorescence properties



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ARTICLE INFO	A B S T R A C T
Keywords: Phenanthrene imidazole Solvatochromism Multi-linear regression analysis Density function theory	A series of highly fluorescent blue-green emitting phenanthrene and 3,6-diphenylphenanthrene based com- pounds have been synthesized to study the effect of different electron donating groups on photophysical properties. A very unique and different fluorescence properties are observed in the case of N-phenyl carbazole donor based compounds as compared to the other electron donating groups. Observed intramolecular charge transfer and highly polar excited states of these compounds are elucidated by Lipert-Mataga correlations. The positive and negative solvatochromism observed from non-polar to polar solvents is also supported using Kamlet-Taft and Catalan multilinear regression analysis. Comparative study of photophysical properties between benzil, phenanthrene and 3,6-diphenylphenanthrene based hydroxyl imidazole derivatives is presented to study the effect of rigidity and extended conjugation. Observed experimental results are also correlated theoretically

using Density Functional theory computations.

1. Introduction

Due to its rigid, conjugated aromatic structure phenanthrene based organic compounds are reported to show improved fluorescence properties with excellent thermal stability, long fluorescence lifetime, high quantum yield as well as solid state fluorescence [1–5]. Phenanthrene and related derivatives have been widely applied in the field of organic light emitting devices (OLED), mainly as blue organic light emitting material [6–12]. Number of conjugated organic molecules were recently reported for their high fluorescence quantum yield in solid state without concentration quenching problem [13–17]. By replacing phenyl unit with phenanthrene moiety different near infra red emitting (NIR) emitting dyes were synthesized and reported to show red shifted absorption-emissions as well as high fluorescence quantum yields [18,19].

Excited state intramolecular proton transfer (ESIPT) molecules have attracted much attention in recent years due to their unique photophysical properties such as large Stokes shift with no self absorption and are used as UV photo stabilizers [20], proton transfer lasers [21], photo switches [22] or fluorescent probes [23] and also as potential materials for organic light emitting diodes [24]. However the use of ESIPT compounds is limited due to its low emission efficiency, concentration quenching of the keto emission and environment sensitive spectral change [25].

Phenanthrene based imidazole compounds with hydroxyl group attached on phenyl ring are studied in detail for their ESIPT phenomenon [15,26], while different phenanthrene based imidazole derivatives are reported as charge transfer compounds where phenanthrene unit acts as electron donor while imidazole acts as electron acceptor. Proton coupled electron transfer reactions have attracted much attention due to their biological applications [27–33]. Kasha et al. proved that in such type of compounds emission can occur through all three states i.e. locally excited state, intramolecular charge transfer (ICT) state or proton transfer state and also they can compete with each other [34–36].

We synthesized different phenanthrene based imidazole derivatives using commercially available phenanthrene-9, 10-dione to study the effect of rigidity on ICT as well as ESIPT properties. Further, to find out the effect of elongated conjugation on fluorescence properties, 3 and 6 position of phenanthrene moiety are substituted with the extra phenyl rings. Both by increasing rigidity and extending the conjugation, improved photophysical properties are observed compared to the previously reported benzil based ESIPT compounds [37]. Similar to the benzil derivatives, typically red shifted absorption-emission peaks are observed for N-phenyl carbazole derivatives; probably due to the keto emission which is absent in other derivatives. Fig. 1 represents all the

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https://doi.org/10.1016/j.dyepig.2018.06.020

Received 19 December 2017; Received in revised form 13 May 2018; Accepted 14 June 2018 Available online 20 June 2018

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PIGMENTS



Fig. 1. Structure of the synthesized compounds.



Fig. 2. Photograph of compounds DHPhI, JHPhI, THPhI, CHPhI, DHPPhI, JHPPhI and CHPPhI.

structures of the synthesized derivatives. Compound **DHPhI**, **JHPhI**, **THPhI** and **CHPhI** are based on phenanthrene moiety while compounds **DHPPhI**, **JHPPhI**, **THPPhI** and **CHPPhI** are based on the 3,6-diphenylphenanthrene moiety (see Fig. 2).

2. Experimental section

2.1. Materials and equipments

All the required chemicals were purchased from local supplier, S D Fine Chemicals, Mumbai, India and also from Alfa aesar Ltd and are used as received without any further purification. The solvents used for synthesis and analytical measurements were also obtained from the local suppliers, dried by following standard procedures and distilled prior to use. All the reactions were monitored by TLC (thin layer chromatography) with detection by UV light. Compound purification was obtained by using column chromatography, which was performed on 100-200 mesh silica as the stationary phase. ¹H and ¹³C NMR spectral data were recorded on a 500 MHz Varian Cary Eclipse Australia 500 MHz instrument using TMS as an internal standard. HRMS analysis was done using a QTOF LC/MS spectrometer. The absorption recorded on PerkinElmer UV- visible spectrophotometer Lambda 25 and emission spectra were recorded on Varian Cary Eclipse fluorescence spectrophotometer at room temperature using a 10 mm cuvette with a 2.5 nm slit width. Emission quantum yields were obtained by using 9,10-diphenylanthracene ($\Phi_F = 0.95$ in cyclohexane) as reference standard.

2.2. Synthesis

2.2.1. General procedure for the synthesis of DHPhI, JHPhI, THPhI, CHPhI, DHPPhI, JHPPhI, THPPhI and CHPPhI

Different hydroxyl aldehyde compounds (1 eq) and phenanthrene or 3,6-diphenylphenanthrene diketo compounds (1.1 eq) were dissolved in minimum amount of acetic acid. Ammonium acetate (20 eq) was added and the mixture was refluxed for 4–5 h. After completion the reaction mixture was cooled to room temperature, quenched with water and neutralized with aq. ammonia. The solid precipitated out was

filtered, washed with water and dried well as crude product, which was further purified by using column chromatography (10–40% EtOAc in hexane) to get the pure products.

2.2.1.1. 5-(Diethylamino)-2-(1H-phenanthro[9,10-d]imidazol-2-yl)phenol (DHPhI). Yield = 0.29 g (52%); Melting point = 158–162 °C. ¹H NMR (500 MHz, DMSO-d₆) δ 13.52 (s, 1H), 9.14 (d, J = 8 Hz, 2H), 8.76 (s, 1H), 8.24 (d, J = 8.5 Hz, 2H), 8.00 (t, J = 7.5 Hz, 2H), 7.90 (t, J = 8.5 Hz, 2H), 6.68 (dd, J = 8.5 and 2 Hz, 1H), 6.50 (d, J = 2 Hz, 1H), 3.63–3.67 (q, J = 7 Hz, 4H), 1.39 (t, J = 7 Hz, 6H). ¹³C NMR (126 MHz, DMSO-d₆) δ 172.7, 159.8, 150.6, 128.1, 127.9, 125.9, 124.7, 122.5, 104.2, 98.6, 44.4, 13.3. HRMS (ESI): m/z calcd for (M + H)⁺ C₂₅H₂₃N₃O 383.1919; found 383.1286. Elemental analysis calcd (%); Mol. Formula: C₂₅H₂₃N₃O (C: 78.71, H: 6.08, N: 11.02, O: 4.19; Found: C: 78.93, H: 5.96, N: 11.05, O: 4.04).

2.2.1.2. 9-(1H-Phenanthro[9,10-d]imidazol-2-yl)-1,2,3,5,6,7-

hexahydropyrido[3,2,1-ij]quinolin-8-ol (JHPhI). Yield = 0.35 g (62%); Melting point = 160–164 °C. ¹H NMR (500 MHz, DMSO- d_6) δ 13.43 (s, 1H), 13.39 (s, 1H), 9.09–9.13 (m, 2H), 8.78 (d, *J* = 7.5 Hz, 1H), 8.68 (d, *J* = 7.5 Hz, 1H), 7.96–8.02 (m, 2H), 7.87–7.89 (m, 3H), 3.40–3.44 (m, 4H), 3.01 (t, *J* = 7 Hz, 2H), 2.95 (t, *J* = 7 Hz, 2H), 2.15–2.18 (m, 4H). ¹³C NMR (126 MHz, DMSO- d_6) δ 154.8, 151.8, 145.5, 134.6, 128.1, 128.1, 127.9, 127.8, 126.1, 125.8, 124.8, 124.5, 123.5, 122.6, 122.5, 122.3, 112.9, 107.5, 101.2, 49.9, 49.5, 27.5, 22.5, 21.6, 21.4. HRMS (ESI): *m/z* calcd for (M + H)⁺ C₂₇H₂₃N₃O 406.1919; found 406.0000. Elemental analysis calcd (%); Mol. Formula: C₂₇H₂₃N₃O (C: 79.97, H: 5.72, N: 10.36, O: 3.95; Found: C: 80.43, H: 5.55, N: 10.32, O: 3.67).

2.2.1.3. 5-(Diphenylamino)-2-(1H-phenanthro[9,10-d]imidazol-2-yl)

phenol (*THPhI*). Yield = 0.25 g (76%); Melting point = 233–236 °C. ¹H NMR (500 MHz, DMSO- d_6) δ 13.79 (s, 1H), 13.45 (s, 1H), 9.13–9.15 (m, 2H), 8.71–8.80 (m, 2H), 8.33 (d, *J* = 8.5 Hz, 1H), 7.89–8.00 (m, 4H), 7.63 (t, J = 7.5 Hz, 4H), 7.39–7.41 (m, 6H), 6.88 (dd, J = 8.5 and 2.5 Hz, 1H), 6.71 (d, J = 2.5 Hz, 1H). HRMS (ESI): *m/z* calcd for (M + H)⁺ C₃₃H₂₃N₃O 478.1919; found 478.1900. Elemental analysis



Scheme 1. Synthesis of compounds DHPhI, JHPhI, THPhI, CHPhI, DHPPhI, JHPPhI, THPPhI and CHPPhI.

calcd (%); Mol. Formula: $C_{33}H_{23}N_{3}O$ (C: 83.00, H: 4.85, N: 8.80, O: 3.35; Found: C: 83.33, H: 4.74, N: 8.82, O: 3.10).

2.2.1.4. 3-(1H-Phenanthro[9,10-d]imidazol-2-yl)-9-phenyl-9H-carbazol-4-ol (CHPhI). Yield = 0.26 g (80%); Melting point = 198–201 °C. ¹H NMR (500 MHz, DMSO- d_6) δ 14.00 (s, 1H), 13.77 (s, 1H), 9.31 (s, 1H), 9.14 (d, J = 8.5 Hz, 1H), 9.12 (d, J = 8.5 Hz, 1H), 8.88 (d, J = 8 Hz, 1H), 8.75 (d, J = 8 Hz, 1H), 8.40 (d, J = 7.5 Hz, 1H), 8.07 (t, J = 7.5 Hz, 1H), 7.89–8.01 (m, 7H), 7.82 (t, J = 7.5 Hz, 1H), 7.58–7.66 (m, 3H), 7.13 (s, 1H). ¹³C NMR (126 MHz, DMSO- d_6) δ 158.1, 150.9, 143.2, 141.5, 137.2, 134.7, 130.9, 128.6, 128.5, 128.3, 128.1, 127.9, 127.3, 126.8, 126.4, 126.2, 124.9, 124.6, 123.8, 122.7, 122.6, 122.4, 121.4, 119.9, 118.6, 116.4, 110.4, 108.1, 97.1. HRMS (ESI): m/z calcd for (M + H)⁺ C₃₃H₂₁N₃O 476.1763; found 476.0000. Elemental analysis calcd (%); Mol. Formula: C₃₃H₂₁N₃O (C: 83.35, H: 4.45, N: 8.84, O: 3.36; Found: C: 83.53, H: 4.39, N: 8.85, O: 3.21).

2.2.1.5. 5-(Diethylamino)-2-(6,9-diphenyl-1H-phenanthro[9,10-d]

imidazol-2-yl)phenol (*DHPPhI*). Yield = 0.28 g (51%); Melting point = 162–166 °C. ¹H NMR (500 MHz, DMSO- d_6) δ 9.50 (s, 2H), 8.98 (d, *J* = 8 Hz, 2H), 8.36 (d, *J* = 8.5 Hz, 2H), 8.15–8.24 (m, 6H), 7.79–7.82 (m, 5H), 7.70 (t, *J* = 7 Hz, 2H), 6.76 (s, 1H), 6.65 (s, 1H), 3.67–3.70 (q, *J* = 7 Hz, 4H), 1.42 (t, *J* = 7 Hz, 6H). ¹³C NMR (126 MHz, DMSO- d_6) δ 159.0, 140.7, 139.2, 132.2, 132.1, 129.6, 129.5, 129.4, 129.3, 128.4, 128.2, 123.7, 122.9, 79.9, 79.8, 79.6, 79.4, 46.4, 13.2. HRMS (ESI): *m/z* calcd for (M + H)⁺ C₃₇H₃₃N₃O 534.2545; found 534.2535. Elemental analysis calcd (%); Mol. Formula: C₃₇H₃₁N₃O (C: 83.27, H: 5.86, N: 7.87, O: 3.00; Found: C: 83.39, H: 5.78, N: 7.86, O: 2.95).

2.2.1.6. 9-(6,9-Diphenyl-1H-phenanthro[9,10-d]imidazol-2-yl)-1,2,3,5,6,7-hexahydropyrido[3,2,1-ij]quinolin-8-ol

 $\begin{array}{l} (JHPPhI). \mbox{ Yield} = 0.03 \mbox{ g} (25\%); \ ^1\mbox{H} \mbox{ NMR} \ (500 \mbox{ MHz}, \mbox{ DMSO-} d_6) \ \delta \ 9.48 \\ (s, 2H), 8.96 \ (d, J = 8 \mbox{ Hz}, 2H), 8.33 \ (d, J = 8.5 \mbox{ Hz}, 2H), 8.13-8.22 \ (m, \\ 6H), 7.77-7.80 \ (m, 5H), 7.67 \ (t, J = 7 \mbox{ Hz}, 2H), 3.38-3.42 \ (m, 4H), 3.02 \\ (t, J = 7 \mbox{ Hz}, 2H), 2.93 \ (t, J = 7 \mbox{ Hz}, 2H), 2.13-2.16 \ (m, 4H). \ Elemental analysis calcd (%); \ Mol. \ Formula: \ C_{39}H_{31}N_{3}O \ (C: 83.99, \ H: 5.60, \ N: \\ 7.53, \ O: 2.87; \ Found: \ C: 84.16, \ H: 5.51, \ N: 7.51, \ O: 2.81). \end{array}$

2.2.1.7. 2-(6,9-Diphenyl-1H-phenanthro[9,10-d]imidazol-2-yl)-5-

(*diphenylamino*)*phenol* (*THPPhI*). Yield = 0.26 g (81%); Melting point = 245–248 °C. ¹H NMR (500 MHz, DMSO- d_6) δ 13.45 (s, 1H), 13.18 (s, 1H), 9.17 (s, 2H), 8.53 (s, 2H), 8.01–8.05 (m, 3H), 7.93 (d,

 $\begin{array}{l} J=7.5~{\rm Hz},\,4{\rm H}),\,7.86~({\rm d},\,J=7.5~{\rm Hz},\,1{\rm H}),\,7.48-7.52~({\rm m},\,4{\rm H}),\,7.34-7.40\\ ({\rm m},\,6{\rm H}),\,7.11-7.14~({\rm m},\,5{\rm H}),\,6.60~({\rm dd},\,J=8.5~{\rm and}~2~{\rm Hz},\,1{\rm H}),\,6.43~({\rm d},\,J=2~{\rm Hz},\,1{\rm H}).^{-13}{\rm C}~{\rm NMR}~(126~{\rm MHz},\,{\rm DMSO-}d_6)~\delta~179.2,\,158.9,\,150.3,\\ 150.2,\,147.4,\,146.9,\,140.8,\,139.2,\,137.8,\,136.1,\,130.2,\,129.3,\,128.6,\\ 127.8,\,126.8,\,125.8,\,124.6,\,122.5,\,112.7,\,108.9,\,107.2.~{\rm HRMS}~({\rm ESI}):\,m/\\ z~{\rm calcd}~{\rm for}~({\rm M}\,+\,{\rm H})^+~{\rm C}_{45}{\rm H}_{31}{\rm N}_{3}{\rm O}~630.2545;~{\rm found}~630.2478.~{\rm Elemental}\\ {\rm analysis}~{\rm calcd}~(\%);~{\rm Mol.}~{\rm Formula:}~{\rm C}_{45}{\rm H}_{31}{\rm N}_{3}{\rm O}~({\rm C}:~85.83,\,{\rm H}:~4.96,\,{\rm N}:\\ 6.67,~{\rm O}:~2.54;~{\rm Found}:~{\rm C}:~85.99,~{\rm H}:~4.81,~{\rm N}:~6.69,~{\rm O}:~2.33). \end{array}$

2.2.1.8. 3-(6,9-Diphenyl-1H-phenanthro[9,10-d]imidazol-2-yl)-9-phenyl-(CHPPhI). Yield = 0.27 g9H-carbazol-4-ol (82%); Melting point = 175–179 °C. ¹H NMR (500 MHz, DMSO- d_6) δ 13.62 (s, 1H), 13.45 (s, 1H), 9.13 (s, 1H), 9.09 (s, 1H), 8.96 (s, 1H), 8.62 (d, J = 8 Hz, 1H), 8.45 (d, J = 8.5 Hz, 1H), 8.06–8.10 (m, 2H), 7.94 (d, J = 7.5 Hz, 3H), 7.88 (d, J = 7.5 Hz, 2H), 7.66 (t, J = 7.5 Hz, 2H), 7.47-7.58 (m. 7H), 7.27–7.41 (m, 5H), 6.80 (s, 1H), ¹³C NMR (126 MHz, DMSO-d₆) δ 157.8, 150.8, 142.8, 141.3, 140.9, 140.8, 137.8, 137.6, 136.9, 134.4, 130.6, 129.3, 128.7, 128.5, 128.3, 127.7, 127.0, 126.7, 126.6, 126.5, 125.8, 125.2, 123.6, 123.1, 122.7, 122.6, 122.4, 121.6, 121.1, 119.6, 118.3, 116.2, 110.1, 107.8, 96.6. HRMS (ESI): *m/z* calcd for (M + H)⁺ C45H29N3O 628.2389; found 628.2322. Elemental analysis calcd (%); Mol. Formula: C₄₅H₂₉N₃O (C: 86.10, H: 4.66, N: 6.69, O: 2.55; Found: C: 86.29, H: 4.53, N: 6.73, O: 2.41).

3. Result and discussion

3.1. Discussion of synthesis

Electron donating hydroxyl aldehyde such as julolidine hydroxyl aldehyde was synthesized by using the reported procedure [38], while triphenylamine and N-phenyl carbazole based hydroxyl aldehydes were synthesized using procedures reported from our group [37]. We synthesized derivatives such as DEMAP hydroxyl phenanthrene imidazole (**DHPhI**), julolidine hydroxyl phenanthrene imidazole (**JHPhI**), triphenylamine hydroxyl phenanthrene imidazole (**THPhI**) and carbazole hydroxyl phenanthrene imidazole (**CHPhI**) by reacting all available aldehydes with commercially available phenanthrene-9,10-dione in ammonium acetate and acetic acid (Scheme 1). To study the effect of extra phenyl rings at 3, 6 position of phenanthrene-9, 10-dione, 3, 6-dibromophenanthrene-9, 10-dione (intermediate 1) was synthesized by reacting phenanthrene-9, 10-dione with bromine in nitrobenzene (Scheme S1 in the supporting information). Further desired intermediate 2 was synthesized by reacting compound 3,6-



(a) 4-(diethylamino)-2-hydroxybenzaldehyde, NH₄OAc / Acetic acid, 120 °C, 2 hrs. (b) Julolidine-2-hydroxybenzaldehyde, NH₄OAc / Acetic acid, 120 °C, 2 hrs. (c) 4-(diphenylamino)-2-hydroxybenzaldehyde, NH₄OAc/Acetic acid, 120 °C, 2 hrs (d) 4-hydroxy-9-phenyl-9*H*-carbazole-3-carbaldehyde, NH₄OAc/Acetic acid, 120 °C, 2 hrs.

Fig. 3. Absorption (a) and emission (b) spectra of DHPhI, JHPhI, THPhI and CHPhI in THF solvent.

Table 1	
Photophysical properties of all compounds in THF solvent.	

Solvent λ_{abs}		$arepsilon_{ m max} imes 10^4$	fwhm	$\lambda_{\rm ems}$	Stokes shif	Stokes shift		f	μ_{eg}
(nm)	$(M^{-1} cm^{-1})$	(nm)	(1111)	(nm)	(cm ⁻¹)			(debye)	
DHPhI	355	3.9	77	425	70	4639	0.63	0.90	8.26
JHPhI	367	3.56	52	439	72	4469	0.43	0.80	7.89
THPhI	386	5.26	46	420	34	2097	0.91	1.11	9.55
CHPhI	381	3.83	85	504	123	6405	0.91	0.82	8.17
DHPPhI	362	5.17	111	431	69	4422	0.51	1.95	12.27
JHPPhI	367	2.95	123	454	87	5222	0.55	1.20	9.70
THPPhI	398	6.38	91	420	22	1316	0.93	1.62	11.73
CHPPhI	392	3.85	66	506	114	5747	0.98	1.08	9.48

dibromophenanthrene-9,10-dione with phenyl boronic acid using Suzuki coupling reaction conditions, which was further reacted with all four different hydroxyl aldehydes to acquire derivatives **DHPPhI**, **JHPPhI**, **THPPhI and CHPPhI** in good yields (Scheme 1).

3.2. Photophysical properties

To study the effect of different electron donating groups on absorption and emission properties of phenanthene based imidazole derivatives in different solvent, we recorded the absorption as well as emission spectra of all these newly synthesized derivatives in solvents of different dielectric constants. The comparative absorption as well as emission spectra of all phenanthrene based ESIPT imidazole derivatives in THF solvent are represented in Fig. 3. Due to their structural similarity, compound **DHPhI** and **JHPhI** are exhibiting similar type of absorption spectra, while same is true for compound **THPhI** and **CHPhI**. Compound **CHPhI** typically exhibited one extra high energetic absorption peak for its rigid carbazole unit (Fig. 3a). Low energetic sharp absorption peak observed for all compounds at around 380 nm can be attributed to the intramolecular charge transfer (ICT) peak, which gets dominated in THPhI and CHPhI compounds for their better intramolecular charge transfer ability over DHPhI and JHPhI derivatives. Comparatively sharper absorption peaks as well as high molar extinction coefficients were observed for compounds THPhI and CHPhI than compounds DHPhI and JHPhI, which show typically broad absorption peaks. In their emission spectra (Fig. 3b), compound DHPhI, JHPhI and THPhI are blue emitting compounds and exhibited emission λ_{max} values at 425, 439 and 420 nm respectively, while compound CHPhI is green emitting compound and emits at 504 nm. Compound THPhI shows comparatively very high emission intensity than other three derivatives due to effective charge transfer from the triphenylamine donor. In all these derivatives as proton transferring OH group is present in vicinity with the proton acceptor imidazole nitrogen, dual emission peaks for their keto tautomer was expected, but they exhibited single emission peaks in non-polar as well as polar solvents. Exceptionally highly red shifted emission peak at 503 nm observed for compound **CHPhI** with 6405 cm⁻¹ Stokes shift, which can be attributed to its keto tautomer formed in the excited state (Table 1). Fig. 4 represents combined normalized absorption and emission spectra of compounds DHPhI, JHPhI, THPhI and CHPhI in THF solvents, where

Table 2

Photophysical properties of DHPhI in all solvent
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Solvent	λ _{abs}	λ_{abs}	$\varepsilon_{ m max} imes 10^4$	fwhm	λ_{ems}	Stokes shif	ft	$\Phi_{\rm F}$	f	μ_{eg}
	(nm)	$(M^{-1} cm^{-1})$	(nm)	(nm)	(nm)	(cm ⁻¹)			(debye)	
Hexane	356	3.8	80	407	51	3519	0.58	0.88	8.16	
Toluene	361	4.0	77	412	51	3428	0.38	0.93	8.47	
THF	355	3.9	77	425	70	4639	0.63	0.90	8.26	
DCM	360	4.0	73	428	68	4413	0.14	0.93	8.43	
MeOH	352	4.2	75	433	81	5314	0.32	0.96	8.49	
Acetonitrile	355	4.1	75	446	91	5747	0.39	0.93	8.39	
DMSO	359	4.1	75	454	94	5780	0.51	0.99	8.72	

compounds **DHPhI**, **JHPhI** and **THPhI** exhibited small Stokes shift of 4639 cm^{-1} , 4469 cm^{-1} and 2097 cm^{-1} , while compound **CHPhI** exhibited large Stokes shift of 6405 cm^{-1} (see Table 2).

We further extended the conjugation of phenanthrene moiety by substituting its 3, 6 position hydrogen atoms with phenyl rings to acquire derivatives such as DHPPhI, JHPPhI, THPPhI and CHPPhI. Fig. 5 represents their comparative absorption and emission spectra in THF solvents. In their absorption spectra, same type of scenario as like compounds DHPhI, JHPhI, THPhI and CHPhI was observed, except one additional high energetic peak was observed for the extra phenyl rings at 3, 6 position of phenanthrene moiety of these compounds. Hence compound CHPPhI exhibited total four absorption peaks (Fig. 5a) as compared to the three absorption peaks of compound CHPhI. Compounds DHPPhI and JHPPhI exhibited very broad absorption spectra than comparatively sharper absorption spectra observed for compound THPPhI and CHPPhI. In their emission spectra again compound CHPPhI exhibited highly red shifted emission peak for its keto tautomer with highest emission intensity than other three derivatives (Fig. 5b).

3.3. Effect of solvents on absorption and emission spectra

The polarity of organic solvents strongly affects the excited state of donor-acceptor compounds; hence we studied absorption and emission spectra of these compounds in different non-polar to polar solvents. Fig. 6 represents absorption and emission spectra of **DHPhI** in different solvents. When we go from non-polar to polar solvents, slightly red shift in their absorption spectra and highly red shifted emission spectra were observed suggesting that the excited state is more stabilized by polar solvents than ground state. The values of molar extinction coefficient, Stokes shift, oscillator strength and transition dipole moment are slightly increased when we go from non-polar to polar solvents for all compounds (Table 2, S1 to S7). Fig. S1 to S7 represents the absorption and emission spectra of compound **JHPhI**, **THPhI**, **CHPhI**, **DHPPhI**, **JHPPhI** and **CHPPhI** in all solvents. Compounds **DHPhI**, **JHPhI**, **DHPPhI** and **JHPPhI** exhibited very good positive solvato-chromism in their emission spectra. Compounds **THPhI** and **THPPhI**



Fig. 5. Absorption (a) and emission (b) spectra of DHPPhI, JHPPhI, THPPhI and CHPPhI in THF solvent.

exhibited very slight positive solvatochromism while compounds CHPhI and CHPPhI exhibited negative solvatochromism i.e. blue shift from non-polar to polar solvent in their emission spectra. Fig. 7 represents emission spectra of compounds DHPhI, JHPhI, THPhI and CHPhI in different solvents. It is observed that derivatives containing DEMAP and Julolidine aldehyde i.e. DHPhI and JHPhI exhibited quenching of fluorescence from non-polar to polar solvents, while triphenyl and carbazole based derivatives such as THPhI and CHPhI, no quenching of fluorescence from non-polar to polar solvents was observed. Similar types of emission spectra were observed for remaining derivatives such as DHPPhI, JHPPhI, THPhI and CHPPhI. In general all these derivatives exhibited very high fluorescence quantum yield in non-polar solvents such as hexane, toluene and THF.



Fig. 4. Combined normalized absorption and emission spectra of compounds DHPhI, JHPhI, THPhI and CHPhI in THF solvent.

Fig. 6. Absorption (a) and emission (b) spectra of DHPhI in different solvents.

Fig. 7. Emission spectra of (a)DHPhI, (b)JHPhI, (c)THPhI and (d)CHPhI in different solvents.

3.4. Solvatochromism and Lippert-Mataga analysis

Fig. 8 represents normalized emission spectra of compounds DHPhI, JHPhI, THPhI and CHPhI in all solvents. We observed positive solvatochromism for compound DHPhI, JHPhI and THPhI, while negative solvatochromism for compound CHPhI from non-polar to polar solvents. This can be correlated with the presence of keto tautomer emission in CHPhI, while enol tautomer emission in all remaining three derivatives. Negative solvatochromism is already reported for the compounds which demonstrate ESIPT process [37]. Rigidized donor derivative (JHPhI) exhibited very large positive solvatochromism (85 nm) and the triphenylamine donor derivative (THPhI) exhibited a very small positive solvatochromism of 21 nm. Quenching of fluorescence from non-polar to polar solvent with positive solvatochromism was observed for compound DHPhI and JHPhI, can be correlated with the twist of the molecule in the excited state to exhibit twisted intramolecular charge transfer (TICT) state. In the case of compound THPhI no any quenching of fluorescence was observed from non-polar

to polar solvents; hence it can be presented as the example of intramolecular charge transfer (ICT). Again similar type of scenario was observed for compound **DHPPhI**, **JHPPhI**, **THPPhI** and **CHPPhI**, where highest positive solvatochromism (83 nm) is observed for **JHPPhI** and negative solvatochromism is observed for compound **CHPPhI** (23 nm).

Very small red shift in the absorption spectra but highly red shifted emission spectra of these compounds, suggest that the excited state of these compounds (except **CHPhI** and **CHPPhI**) is highly stabilized as compared to the ground state by the polar solvents and opposite is true for the compounds **CHPhI** and **CHPPhI**, which shows negative solvatochromism. Hence the role of dielectric constant as well as refractive index of the solvents is very important for the observed shift in emission spectra from non-polar to polar solvents. Consequently we also observed gradual increase in Stokes shift with the increased solvent polarity and which can be correlated by using Lippert-Mataga equation. According to Lippert-Mataga correlation physical parameters such as dielectric constant and refractive index are directly correlated with the observed Stokes shift. It is very general equation and does not account

Fig. 8. Normalized emission spectra of compound DHPhI, JHPhI, THPhI and CHPhI (positive and negative solvatochromism).

Fig. 9. Lippert-Mataga correlations between Stokes shift and Lippert-Mataga function (Δf) for compounds DHPhI, JHPhI, THPhI and CHPhI.

Fig. 10. Lippert-Mataga correlations between Stokes shift and Lippert-Mataga function (Δf) for compounds **DHPPhI**, **JHPPhI**, **THPPhI** and **CHPPhI**.

any specific solute-solvent interactions such as hydrogen bonding. Figs. 9 and 10 represent the plots of λ shift vs. Lippert-Mataga function (Δf_{LM}). It shows linear relationship suggesting that the solvent parameters such as dielectric constant and refractive index are collectively responsible for the observed shift in the emission spectra. For compounds **DHPhI**, **JHPhI**, **THPhI**, **DHPPhI**, **JHPPhI** and **THPPhI** Stokes shift increases with the increasing Lippert-Mataga function (Δf_{LM}) i.e. increasing solvent polarity as well as refractive index. In contrast due to the presence of keto tautomer in the excited state (ESIPT effect), compounds such as **CHPhI** and **CHPPhI** shows decreased Stokes shift values with the increasing Lippert-Mataga function and they are also showing very good linear relationship of Stokes shift with the Lippert-Mataga function (Δf_{LM}).

3.5. Multilinear regression analysis of observed spectral shift in absorption and emission spectra using Kamlet-Taft and Catalan parameters

In general linear correlation parameters such as Lippert-Mataga, Mac-Rae or E_T^N (30) are used to understand the effect of solvent polarity on the observed absorption and emission spectra shift, but these parameters are not explaining precisely which solvent parameters such as solvent acidity, basicity, dipolarity or polarizability are responsible for the observed spectral shift. Hence multilinear approach is proposed by Kamlet and Taft [39,40] as represented in equation (1)

$$y = y_0 + a_{\alpha} \alpha + b_{\beta} \beta + c_{\pi^*} \pi^*$$
 (1)

where, 'y' is the solvent affected physiochemical property (e.g. absorption maxima (\bar{u}_{abs}), emission maxima (\bar{u}_{emi}), Stokes shift ($\Delta \bar{u}$), etc.). 'y₀' is the studied physiochemical property in the gas phase, while *a*, *b*, *c* and *d* are adjustable coefficients which reflect the dependence of 'y' to the various solvent parameters such as α (effect of acidity of solvent), β (effect of basicity of solvent) and π^* (collective effect of solvent polarity/dipolarity and polarizability). However if solvent acidity and basicity are not affecting the value of y, then among solvent polarity and polarizability it is difficult to sort out which factor is exactly influencing the studied physiochemical property y, hence Catalan [41–43] proposed another expression as represented in equation (2)

$$y = y_0 + a_{SA}SA + b_{SB}SB + c_{SP}SP + d_{SdP}SdP$$
(2)

where, Catalan utilized same solvent parameters i.e. solvent acidity (SA) and solvent basicity (SB) which already utilized by Kamlet and Taft, but he divided the last parameter proposed by Kamlet and Taft i.e. π^* into two separate parameters i.e. solvent polarizability (SP) and solvent dipolarity (SdP). Since the Kamlet-Taft parameters are well established and Catalan parameters are the modified version of it, we used both these approaches simultaneously to understand exactly which factor is mostly affecting the observed spectral shift in absorption and emission spectra as well as increased or decreased Stokes shift from non-polar to polar organic solvents for all these imidazole derivatives. Reported Kamlet-Taft [44] and Catalan [45] parameters are used for the analysis of observed spectral shift in absorption, emission and Stokes shift from non-polar to polar solvents.

Table 3 represents multilinear analysis of absorption maxima (\bar{u}_{abs}), emission maxima (\bar{u}_{emi}) and Stokes shift ($\Delta \bar{u}$) for **CHPhI** in different organic solvents were carried out by using both Kamlet-Taft (2) and Catalan (3) parameters. Absorption spectra analysis of this compound exhibited comparatively higher correlation coefficient by Catalan method (0.98) than that obtained by Kamlet-Taft method (0.23). We observed slightly red shifted absorption spectra from non-polar to polar solvents, hence negative estimated coefficient was expected, which was observed only for solvent polarizability factor (d_{SP}) by Catalan method with highest value of estimated coefficient (1.62) and minimum

Table 3

Estimated coefficients (y₀, a, b, c, d), their standard errors and correlation coefficients (r) for the multi-linear analyis of (\bar{u}_{abs}) , (\bar{u}_{emi}) and $(\Delta \bar{u})$ of compound CHPhI as a function of Kamlet-Taft (1) and Catalan (2) solvent scales. Where, α or SA for solvent acidity, β or SB for solvent basicity, π^* for collective parameter of solvent dipolarity and polarizability according to Kamlet-Taft equation, SdP and SP for solvent dipolarity and polarizability respectively according to Catalan equation.

Kamlet-Taft	$y_0 \times 10^3$	a _α	b_{β}	c_{π^*}		r
Ū _{abs} Ū _{emi} ΔŪ	$\begin{array}{r} 26.18 \ \pm \ 0.11 \\ 19.78 \ \pm \ 0.07 \\ 6.40 \ \pm \ 0.11 \end{array}$	$\begin{array}{rrrr} 0.25 \pm 0.16 \\ 0.78 \pm 0.10 \\ -0.53 \pm 0.16 \end{array}$	$\begin{array}{rrrr} 0.18 \ \pm \ 0.28 \\ 0.06 \ \pm \ 0.18 \\ 0.12 \ \pm \ 0.29 \end{array}$	-0.20 ± 0.25 0.08 ± 0.17 -0.20 ± 0.26		0.23 0.92 0.62
Catalan	$y_0 imes 10^3$	a _{SA}	b _{SB}	c _{SdP}	d _{SP}	r

standard error (0.12), hence this can be considered as the main factor responsible for the slightly red shifted absorption spectra. It was further confirmed by the plot of absorption values (\bar{u}_{abs}) with each individual solvent parameter.

Multilinear regression analysis of emission spectra of CHPhI exhibited very high values of correlation coefficients by both Kamlet-Taft (0.92) and Catalan (0.86) methods. As we observed blue shifted emission spectra for this compound experimentally from non-polar to polar solvents, positive estimated coefficients are expected. Though we observed positive values for all solvent parameters by Kamlet-Taft method, only solvent acidity (a_{SA}) and solvent dipolarity (c_{SdP}) parameters show positive value for their estimated coefficients by Catalan method. Hence parameters such as solvent basicity (b_{SB}) and solvent polarizability (d_{SP}) can be neglected from the discussion as they showed negative estimated coefficients. Among solvent acidity (a_{SA}) and solvent dipolarity (c_{SdP}) solvent parameters, higher estimated coefficient (1.07) and minimum standard error (0.28) is observed for solvent acidity parameter as compared to the solvent dipolarity parameter, hence it can be considered as the main factor responsible for the blue shifted emission spectra from non-polar to polar solvents. It was further confirmed by plotting emission values ($\bar{\upsilon}_{emi}$) individually with solvent acidity and solvent dipolarity parameters.

Table S8 and S9 represents multilinear analysis of absorption maxima (\bar{u}_{abs}), emission maxima (\bar{u}_{emi}) and Stokes shift ($\Delta \bar{u}$) for all remaining compounds in different solvents by using both Kamlet-Taft (2) and Catalan (3) parameters. All remaining compounds showed higher values of their correlation coefficient for the analysis of absorption spectra by Catalan method than that by Kamlet-Taft method. All the compounds exhibited highest negative estimated coefficient and minimum standard error for the solvent polarizability factor (d_{SP}) in comparison with the all other factors, hence this can be considered as the main factor responsible for the slightly red shifted absorption spectra. In the case of their emission spectra, solvent acidity (a_{SA}) is emerged out as the main factor responsible for the blue shifted emission spectra of CHPPhI from non-polar to polar solvents, while solvent dipolarity (c_{SdP}) is emerged out as the main factor responsible for the red shifted emission spectra of compounds DHPhI, JHPhI, THPhI, DHPPhI, JHPPhI and THPPhI from non-polar to polar solvents.

The graph plotted for the predicted emission data obtained by Kamlet-Taft method with the experimental data for all compounds show very good linear fit with slope of 0.79, 0.84, 0.95 and 0.96 for compounds **DHPhI**, **JHPhI**, **THPhI** and **CHPhI**, while 0.69, 0.76, 0.92 and 0.95 for compounds **DHPPhI**, **JHPPhI**, **JHPPhI**, **THPPhI** and **CHPPhI** respectively (Fig. 11).

3.6. Photostability study

Photostability study of compounds **DHPhI**, **JHPhI**, **THPhI** and **CHPhI** was carried out under UV light at different time intervals. $10 \,\mu$ M solutions of these compounds in toluene solvent were irradiated at 254 nm up to 150 min. Both absorption as well as emission spectra of

Fig. 11. Correlation between experimental and predicted emission wave number for DHPhI (a), JHPhI (b), THPhI (c), CHPhI (d), DHPPhI (e), JHPPhI (f), THPPhI (g) and CHPPhI (f) by Kamlet-Taft method.

these compounds was recorded at each 30 min time interval. Fig. 12 and Fig S8 to S10 represent absorption and emission spectra of compound JHPhI and DHPhI to CHPhI from 0 to 150 min time interval respectively. We found these compounds highly photostable under UV light as no remarkable change in their absorption as well as emission intensity is recorded up to 150 min time interval. Comparatively compound JHPhI exhibited high photostability, while compound DHPhI less photostability under UV light.

3.7. Comparative photophysical parameters of benzil, phenanthrene and 3,6-diphenylphenanthrene based compounds

Rigidity and extended conjugation are two important factors responsible for the improved photophysical properties in the case of fluorescent donor-acceptor compounds. Benzil based free rotating ESIPT compounds and their detail photophysical properties were reported from our group recently [37]. We compared photophysical properties of benzil, phenanthrene (rigidized structure) and 3,6-diphenylphenanthrene (extended conjugation) as represented in Table 4.

Fig. 13 and Fig. 14 represents normalized absorption and emission spectra of compounds **CHPI**, **CHPhI** and **CHPPhI** in THF solvent. It can be observed that when we go from flexible benzil derivative **CHPI** towards more rigid derivative phenanthrene and 3,6-diphenylphenanthrene red shifted absorption as well as emission peaks were observed. Overall all photophysical parameters including quantum yield, oscillator strength (f) and transition dipole moment (μ_{eg}) are improved for rigid phenanthrene based compounds than flexible benzil based compounds.

Fig. 12. Absorption (a) and emission (b) spectra of compound JHPhI under UV light up to 150 min.

Table 4

Photophysical properties of CHPI, CHPhI and CHPPhI in THF solvent.

Solvent	lvent λ_{abs} $\varepsilon_{max} \times 1$		fwhm	fwhm λ_{ems}		Stokes shift		f	μ_{eg}
	(1111)	$(M^{-1} cm^{-1})$	(nm)	(1111)	(nm)	(cm ⁻¹)			(debye)
CHPI CHPhI CHPPhI	365 381 392	1.52 3.83 3.85	27 85 66	489 504 506	124 123 114	6947 6405 5747	0.85 0.91 0.98	0.67 0.82 1.08	7.19 8.17 9.48

Fig. 13. Normalized absorption spectra of compounds CHPI, CHPhI and CHPPhI.

Fig. 14. Normalized emission spectra of compounds CHPI, CHPhI and CHPPhI.

Fig. 15. Comparative normalized emission spectra of triphenylamine based compounds (THPI, THPPhI, THPPhI) and carbazole based compounds (CHPI, CHPPhI).

Fig. 16. Optimized geometries of THPPhI and CHPPhI in their ground and excited state in THF solvent.

3.8. Shift in emission spectra between triphenylamine and N-phenyl carbazole attached benzil, phenanthrene and 3,6-diphenylphenanthrene based compounds

Fig. 15 represents normalized emission spectra of compounds THPI, THPhI, THPPhI and CHPI, CHPPI, CHPPhI in THF solvent. In general little red shift in the emission spectra is observed when benzil and phenanthrene based compounds are compared, while opposite is true for the triphenylamine and N-phenyl carbazole based compounds. Triphenylamine based compounds i.e. THPI, THPHI and THPPHI exhibited their emission spectra in the blue region i.e. from 401 nm to 420 nm, while N-phenyl carbazole based compounds i.e. CHPI, CHPHI and CHPPHI emitted in the bluish green region i.e. from 489 nm to 506 nm. Very slight modification in the structure of electron donating group resulted into large difference in their emission spectra and almost

Fig. 18. HOMO-LUMO FMO diagrams of compound DHPhI, JHPhI, THPhI and CHPhI in THF solvent.

100 nm shift in emission spectra is observed. This is mainly attributed to the combined effect of rigidity as well as excited state intramolecular charge transfer (ESIPT). When we go from non-polar to polar solvents slight red shift in their emission spectra is observed for triphenylamine based compounds, while blue shift is observed for N-phenyl carbazole based compounds as represented in Fig. 8.

3.9. Optimization of structures by TD-DFT method

To understand the molecular geometries in detail, all the derivatives were optimized by Time-dependent density functional theory (TD-DFT) using 6-31G (d) basis set with B3LYP functional [46–48] in gas phase as well as THF solvent. Fig. 18 and 19 represents their frontier molecular orbital pictures at HOMO and LUMO level. At their HOMO level, electron density is mainly located on the electron donating *N*,*N* diethyl aniline, julolidine, triphenylamine or N-phenyl carbazole phenyl rings, while on the imidazole heterocycles fused with phenanthrene rings at their LUMO level. As the N-phenyl ring of carbazole based derivatives such is **CHPhI** and **CHPPhI** is perpendicular to the main carbazole unit, no any electron density was observed on the N-phenyl ring at their HOMO level. Comparatively better energy transfer from donor to acceptor can be expected in the case of compounds **DHPPhI**, **JHPPhI**, **THPPhI** and **CHPPhI** than their phenanthrene based counterparts because minimum overlap between the electron densities between their

Fig. 17. HOMO-LUMO energy gaps of compounds CHPhI, DHPhI, JHPhI and THPhI in THF solvent.

Fig. 19. HOMO-LUMO FMO diagrams of compound DHPPhI, JHPPhI, THPPhI and CHPPhI in THF solvent.

 Table 5

 Comparative experimental and computational photophysical parameters of all compounds in toluene solvent.

Compound	$\lambda_{abs}{}^a$ nm	$\lambda_{abs}{}^{b}$ nm	$\lambda_{ems}{}^{c}$ nm	\mathbf{f}^{d}	f	$\mu_{eg}{}^f$	$\mu_{eg}{}^g$	%D ^h	Major ⁱ contribution
DHPhI	361	370	412	0.93	0.58	8.47	5.12	2.61	H →L 87.55
JHPhI	369	378.14	419	0.77	0.57	7.76	4.93	2.47	H →L 90.23
THPhI	371	387.4	422	1.01	1.26	9.15	4.22	4.42	H →L 96.91
CHPhI	364	365.65	506	0.89	1.04	8.54	2.91	0.45	H →L 94.87
DHPPhI	367	370.44	417	1.47	0.82	10.73	5.25	6.93	H →L 95.58
JHPPhI	369	401.23	433	1.18	0.76	9.79	4.84	5.31	H →L 96.27
THPPhI	400	403.47	423	1.64	1.39	11.81	4.25	0.87	H →L 92.11
CHPPhI	394	383.64	507	1.2	1.17	10.03	2.95	2.63	H →L 92.75

^a Experimental absorption λ_{max} .

^b Computational vertical excitation.

^c Experimental emission λ_{max} .

^d Experimentally calculated oscillator strength.

^e Computational oscillator strength.

^f Experimentally calculated transition dipole moment.

^g Computational dipole moment.

 $^{\rm h}$ Percent deviation from experimental absorption λ_{max}

ⁱ Major electronic transition.

HOMO and LUMO level was observed for these derivatives.

Fig. 16 represents optimized geometries of compounds THPPhI and CHPPhI in their ground and excited state. Though there is no much difference in dihedral angles observed when we go from ground to excited state for compounds THPPhI and CHPPhI, large difference between the dihedral angle of C27-N-33-C-35-C37 (46.75°) for THPPhI and C28-N-33-C36-C38 (56.99°) for CHPPPhI in their ground state as well as 36.51° and 54.85° in their excited state is observed respectively. Fig. 17 represents HOMO-LUMO energy difference for compounds DHPhI, JHPhI, THPhI and CHPhI. Compound JHPhI exhibits lowest HOMO-LUMO energy difference (3.74 eV), while compound CHPhI exhibits highest one (3.91 eV) in all four compounds, suggesting that effective intramolecular charge transfer is observed in the case of compound JHPhI while opposite is true for compound CHPhI. Instead of the poor intramolecular charge transfer observed for this compound highly red shifted emission peak can be supported by the excited state intramolecular proton transfer (ESIPT) phenomenon. Similar type of trend is observed for compounds DHPPhI, JHPPhI, THPPhI and CHPPhI.

We compared the computationally derived lowest energy transitions i.e. vertical excitations obtained after exciting the ground state optimized compounds up to at least first 10 states with the experimentally observed absorption values in toluene solvent and are having similar trends (Table 5). Similarly we also compared the experimentally observed oscillator strength and dipole moment values with the computationally derived one and observed comparatively lower values of oscillator strength as well as dipole moment than experimental one but with the same trend. Major electronic transitions for all the compounds were found from HOMO to LUMO level (87–96%), in which maximum HOMO-LUMO electronic transition (96.91%) is shown by **THPhI** compound and minimum one (87.55%) by **DHPhI** compound.

4. Conclusion

In conclusion, phenanthrene and 3,6-diphenylphenanthrene based imidazole derivatives were synthesized to study the effect of different electron donating groups on photophysical properties. By extending the conjugation of phenanthrene unit by extra phenyl rings at 3 and 6 positions, red shifted absorption as well as emission peaks and improved quantum yield in different organic solvents were observed. Further, we noted red shifted emissions for **CHPhI** and **CHPPhI** derivatives as compared to the all remaining derivatives due to the extra rigidity by carbazole unit. Negative solvatochromism observed for **CHPhI** and **CHPPhI** derivatives can be supported by the dominating excited state intramolecular proton transfer process in these compounds while positive solvatochromism observed for all remaining compounds from non-polar to polar solvents can be supported by the dominant intramolecular charge transfer process. Quenching of fluorescence from non-polar to polar solvents is observed for all DEMAP and julolidine based imidazole derivatives but no fluorescence quenching is observed for triphenylamine and N-phenyl carbazole based derivatives. Multilinear regression analysis of these compounds is carried out using Kamlet-Taft and Catalan factors and concluded that solvent acidity (a_{SA}) is the main factor responsible for the blue shifted emission spectra of compounds **CHPhI** and **CHPPhI**, while solvent dipolarity (c_{SdP}) is the main factor responsible for the red shifted emission spectra of all other derivatives from non-polar to polar solvents. We also optimized their structures using TD-DFT method to correlate our experimental finding and found good match between the experimental and computational results.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx. doi.org/10.1016/j.dyepig.2018.06.020.

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