Electronic Supporting Information

Single-Component White-light Emission via Intramolecular Electronic Conjugation-truncation with Perylenemonoimide

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General

Unless otherwise mentioned, reactions were performed in oven-dried glassware under a nitrogen atmosphere and stirred with Teflon-coated magnetic stirring bars. Tetrahydrofuran was distilled over sodium/ benzophenone ketyl. All other solvents and reagents were used as received from Sigma-Aldrich USA unless otherwise mentioned. Reaction temperatures above ambient condition (298 K) refer to oil bath temperature. Thin layer chromatography was performed using Merck Silica gel 60 F-254 pre-coated plates and visualized using UV irradiation (\(\lambda=254/365\) nm). Silica gel from Merck (particle size 100-200 mesh) was used for column chromatography. \(^1\)H and \(^{13}\)C NMR spectra were recorded on Bruker 500 MHz spectrometers with operating frequencies of 125 MHz for \(^{13}\)C. Chemical shifts (\(\delta\)) are reported in ppm relative to the residual solvent signal (CDCl\(_3\), \(\delta = 7.26\) for \(^1\)H NMR and \(\delta = 77.0\) for \(^{13}\)C NMR). High resolution mass spectrometry (HRMS) data were recorded on MicrOTOF-Q-II mass spectrometer using APCI mode.

Instrumentation and methodology

Steady state absorption and fluorescence measurement:

Steady state absorption measurement was performed using Cary 5000 Spectrophotometer from Agilent Technologies using 1 cm path length quartz cuvette. All solvent dependent steady-state fluorescence measurements were carried out using HORIBA Jobin Yvon Fluorolog fluorimeter using Origin 8 software provided with the instrument. A dilute solution of the sample was taken for all the measurements to keep the absorption value bellow the limit of inner filter effect. Fluorescence spectra were recorded using 1 cm path length quartz cuvette and keeping both excitation and emission slit at 2 nm. All the experiments were carried out at ambient temperature (298 K) otherwise mentioned.

Time resolved measurement:

Time-resolved fluorescence measurements were performed using a Hamamatsu MCP photomultiplier (R-3809U-50). The time-correlated single photon counting (TCSPC) setup consists of an Ortec 9327 pico-timing amplifier and using pulse Diode laser (\(\lambda_{ex}\) 370 nm and 510 nm) with fwhm ~175 ps and ~ 210 ps respectively with a setup target 10,000 counts. The instrument response function (IRF) was measured before and after fluorescence lifetime measurement using a dilute suspension of Ludox (purchased from Sigma) colloidal silica. The emission polarizer was positioned at magic angle (54.7 \(^\circ\)) polarization with respect to excitation polarizer. Fitting function was employed by iterative
deconvolution method using supplied software DAS v6.2. The quality of the fitted data was judged from the reduced chi-squared value ($\chi^2$), calculated using the IBH software provided with the instrument. All the measurements were carried out at ambient temperature (298 K).

**Scanning Electron Microscopy (SEM):**

The solution of PMIA$^+$ and its nanoparticle in respective solvent were drop cast on a glass cover-slip and coated with gold by sputter coating for 2 min. They were visualised under a scanning electron microscope from Carl Zeiss at a working voltage of 5.0 kV.

**Synthetic procedure:**

![8-bromo-2-(2-ethylhexyl)-1H-benzo[10,5]anthra[2,1,9-def]isoquinoline-1,3(2H)-dione (3)](image)

8-bromo-2-(2-ethylhexyl)-1H-benzo[10,5]anthra[2,1,9-def]isoquinoline-1,3(2H)-dione (3): 2 (1.272 g, 2.934 mmol, was synthesized from 1 as per the reported procedure in *J. Org. Chem.*, 2011, 76, 2386) was dissolved in CH$_2$Cl$_2$ (330 mL), Br$_2$ (380 $\mu$L) was added drop wise. The reaction was stirred at reflux under N$_2$ atmosphere for 2 h. The reaction mixture was cooled to room temperature. Excess Br$_2$ (from Merck) was eliminated by passing N$_2$. Solvent was evaporated using rotary evaporator and the residue was purified by column chromatography (Silica, CHCl$_3$ as eluent) afforded the desire compound (1.199 g, 80 %).$^1$H NMR (500 MHz, CDCl$_3$) $\delta$ = 8.57 (t, $J$=7.9, 1H), 8.45 (d, $J$=7.1, 1H), 8.40 (d, $J$=8.1, 1H), 8.35 (d, $J$=8.1, 1H), 8.30 (d, $J$=8.4, 1H), 8.20 (d, $J$=8.2, 1H), 7.89 (d, $J$=8.1, 1H), 7.75 – 7.68 (m, 1H), 4.14 (ddd, $J$=19.8, 12.9, 7.3, 1H), 1.97 (dt, $J$=13.1, 6.6, 1H), 0.95 (t, $J$=7.4, 2H), 0.89 (t, $J$=7.1, 2H), 0.89 (t, $J$=7.1, 2H).
2-(2-ethylhexyl)-8-((triisopropylsilyl)ethynyl)-1H-benzo[10,5]anthra[2,1,9-def]isoquinoline-1,3(2H)-dione (4): 3 (511 mg, 1.000 mmol), (Triisopropylsilyl)acetylene (246 μL, 1.1 mmol) were taken in a dry Schlenk tube. Toluene (10 ml), triethylamine (2 ml) was added in the reaction mixture. The resulting solution was degassed thrice by freeze pump thaw cycles. Then under N\textsubscript{2} atmosphere Pd\textsubscript{2}(dba)\textsubscript{3} (91.5 mg, 1.1 mmol), P(o-tol)\textsubscript{3} (236 mg, 0.65 mmol) were added in the Schlenk tube. Then reaction mixture was evacuated and flushed with nitrogen twice. Reaction mixture was heated at 65\textdegree C for 18 h and cooled to room temperature. Solvent was evaporated using rotary evaporator and the residue was purified by column chromatography (Silica, CHCl\textsubscript{3} as eluent) afforded the desire compound (480mg, 78 %)

\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \( \delta = 8.52 \text{ (dd, } J=8.0, 5.7, 1H), 8.43 \text{ (d, } J=8.3, 1H), 8.39 \text{ (d, } J=7.1, 1H), 8.33 \text{ (d, } J=8.2, 1H), 8.28 \text{ (dd, } J=15.8, 8.1, 1H), 7.77 \text{ (d, } J=7.9, 1H), 7.70 – 7.62 \text{ (m, } 1H), 4.12 \text{ (ddd, } J=19.8, 12.9, 7.3, 1H), 2.03 – 1.87 \text{ (m, } 1H), 1.40 \text{ (dd, } J=14.1, 6.9, 2H), 1.36 – 1.29 \text{ (m, } 2H), 1.26 – 1.21 \text{ (m, } 10H), 0.95 \text{ (t, } J=7.4, 2H), 0.89 \text{ (t, } J=7.1, 2H).

![Image of compound 4](image4.png)

2-(2-ethylhexyl)-8-ethynyl-1H-benzo[10,5]anthra[2,1,9-def]isoquinoline-1,3(2H)-dione (5): 4 (150 mg, 0.244 mmol) was dissolved in dry THF ( 3 ml ) and stirred for 5 minute at room temp. Then Tetrabutylammonium fluoride solution (1.0 M in THF) (0.732 ml, 0.732 mmole) was added drop wise. Reaction mixture was stirred at room temperature. The progress of the reaction was monitored by TLC. After the completion of the reaction (20 min) distilled water (10 ml) was added and precipitate was filtered out, which was purified by column chromatography (Silica, CHCl\textsubscript{3} as eluent) afforded the desire compound (134 mg, 83 %) \( \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \delta = 8.45 \text{ (d, } J=6.1, 1H), 8.44 \text{ (d, } J=6.1, 1H), 8.33 – 8.29 \text{ (m, } 1H), 8.27 \text{ (d, } J=7.2, 1H), 8.22 \text{ (d, } J=8.1, 1H), 8.17 \text{ (d, } J=8.1, 1H), 8.14 \text{ (d, } J=8.0, 1H), 7.70 \text{ (d, } J=7.8, 1H), 7.64 – 7.55 \text{ (m, } 1H), 4.11 \text{ (ddd, } J=19.8, 12.9, 7.3, 2H), 3.66 \text{ (s, } 1H), 2.03 – 1.89 \text{ (m, } 1H), 1.47 – 1.37 \text{ (m, } 5H), 1.33 \text{ (ddd, } J=16.2, 9.3, 6.2, 5H), 0.95 \text{ (t, } J=7.4, 4H), 0.89 \text{ (t, } J=7.1, 4H).

![Image of compound 5](image5.png)
2-(2-ethylhexyl)-8-(phenanthren-9-yethynyl)-1H-benzo[10,5]anthra[2,1,9-def]isoquinoline-1,3(2H)-dione (6): Compound 5 (16.1 mg, 0.0661 mmol), 9-bromophenanthrene (30 mg, 0.0656 mmol, from Alfa-Aesar) were taken in a dry Schlenk tube. Toluene (2.5 ml), triethylamine (0.5 ml) was added in the reaction mixture. The resulting solution was degassed by freeze pump thaw cycles for three times. Then under N<sub>2</sub> atmosphere Pd<sub>2</sub>(dba)<sub>3</sub> (5.72 mg, 0.0063 mmol), P(o-tol)<sub>3</sub> (12.36 mg, 0.041 mmol) were added in the Schlenk tube. Then reaction mixture was evacuated and flushed with N<sub>2</sub> two times. Reaction mixture was heated at 65<sup>0</sup> C for 18 h and was cooled to room temperature. Solvent was evaporated using rotary evaporator. The residue was purified by coloumn chromatography (Silica, CHCl<sub>3</sub> as eluent) afforded the desire compound (16.8 mg, 40%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ = 8.72 (dd, J=6.6, 2.8, 1H), 8.67 (d, J=8.2, 1H), 8.63 – 8.58 (m, 2H), 8.55 (dd, J=8.0, 2.6, 2H), 8.48 (d, J=7.6, 1H), 8.37 (dd, J=11.9, 8.1, 3H), 8.16 (s, 1H), 7.95 (d, J=7.8, 1H), 7.89 (d, J=7.3, 1H), 7.78 – 7.74 (m, 2H), 7.72 – 7.68 (m, 1H), 7.63 (t, J=6.9, 1H), 4.13 (ddd, J=19.8, 12.9, 7.4, 2H), 1.97 (d, J=6.6, 1H), 1.43 – 1.38 (m, 3H), 1.35 – 1.28 (m, 4H), 0.95 (t, J=7.4, 3H), 0.89 (t, J=7.1, 3H). Elemental analysis: found - C, 86.91 %; H, 5.48 %; N, 2.17 %; calc. for C<sub>46</sub>H<sub>35</sub>NO<sub>2</sub> - C, 87.17 %; H, 5.57 %; N, 2.21 %. Calculated mass-633.2668; mass obtained [M+H]= 634.2711.

Figure S1: Solvent dependent fluorescence spectra of PMIAP.
**Figure S2**: Solvent dependent absorption spectra of PMIAP.

**Figure S3**: Fluorescence decay profile of PMIAP in monomer (in THF, $\tau_{\text{avg}}=3.5$ ns, $\lambda_{\text{mon}}=570$ nm), aggregated (MeOH, $\tau_{\text{avg}}=2.7$ ns $\lambda_{\text{mon}}=620$ nm) and nanoparticle ( $\tau_{\text{avg}}=3.9$ ns, $\lambda_{\text{mon}}=460$ nm).
Figure S4: Concentration dependent absorption spectra of PMIAP in (a) chloroform and (b) methanol and the aggregation-induced deviation from Beer-Lambert law in (c) chloroform and (d) methanol.
**Figure S5**: Concentration dependent NMR spectra of PMIAP in CDCl$_3$ showing upfield chemical shift upon increasing concentration.

**Figure S6**: Concentration dependent kinetic profile of nanoparticle formation PMIAP in THF.
Figure S7: Solvodynamic size of self-assembled PMIAP nanoparticle after overnight incubation. The average size obtained is $\langle 100 \pm 14 \rangle$ nm.

Figure S8: Spectral overlap of the absorption spectra and the emission spectra of perylene monomide in THF.
Figure S9: Fluorescence lifetime decay in THF of (a) PMIAP and its mixture with nanoparticle (NP) solutions (λ<sub>ex</sub>=470 nm, λ<sub>mon</sub>=570 nm); (b) NP solution and mixture with PMIAP (λ<sub>ex</sub>=373 nm, λ<sub>mon</sub>=460 nm)

Figure S10: Effect of sonication (30 min., 30 kHz) on nanoparticle of PMIAP in THF.
**Figure S11:** Nanoparticle of PMIAP dried and dissolved in other solvent.

**Figure S12:** Fluorescence spectra of PMIAP in different time in THF.
**Figure S13:** Fluorescence spectra of mixture of nanoparticle and monomer of PMIAP in THF.

**Figure S14:** Fluorescence spectra of nanoparticle in solid-state.
Figure S15: $^1$H NMR spectra of 3 in CD$_3$Cl.
Figure S16: ¹H NMR spectra of 4 in CD₃Cl.
Figure S17: $^1$H NMR spectra of 5 in CD$_3$Cl.
Figure S18: $^1$H NMR spectra of 6 in CD$_3$Cl.
Figure S19: $^{13}$C NMR spectra of 6 in CD$_3$Cl.
Figure S20: HRMS (APCI) spectrogram of compound 6.