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Synthesis, self-assembly and Biolabeling of Perylene diimide-Tyrosine Alkyl Amide based Amphiphiles: Nanomolar detection of AOT Surfactant

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Synthetic Detail:

Synthesis of methyl 6-Aminohexanoate hydrochloride

Dissolve 6-Aminocaproic acid (2 g, 0.015 mol) in 60 ml CH₃OH. Keep round bottom flask at 0°C. Then add SOCl₂ (2.77 ml, 0.038 mol) dropwise and continue the reaction on stirring for 10 h at room temperature. After this time interval, the solvent was evaporated and 6-Aminocaproic methyl ester hydrochloride was isolated after triturating the residue with diethyl ether. This triturating procedure was repeated three times to remove the traces of SOCl₂ from whitish precipitate of 6-Aminocaproic methyl ester hydrochloride.

¹**H NMR (400 MHz, DMSO-***d*₆, **25**°**C**) δ 3.57 (s, -OCH₃, 2H), 2.70 (t, J= 8 Hz, 2H), 2.28 (t, *J* = 7.6 Hz, 2H), 1.59 – 1.43 (m, 4H), 1.32 – 1.25 (m, 2H).

¹³C NMR (100 MHz, DMSO-*d*₆, 25°C) δ 173.7, 51.7 (-OCH₃), 38.9, 33.5, 27.0, 25.8, 24.4.



6-aminohexanoic acid

6-methoxy-6-oxohexan-1-aminium chloride

1. Characterization data of Precursors and target derivatives



Figure S1a: ¹H NMR spectrum of 6-aminocaproic methyl ester hydrochloride in DMSO-*d*₆.



Figure S1b: ¹³C NMR spectrum of 6-aminocaproic methyl ester hydrochloride in DMSO-d₆.



Figure S1c: DEPT-135 spectrum of 6-aminocaproic methyl ester hydrochloride in DMSO-d₆.



Figure S2a: ¹H NMR spectrum of 1c in CDCl₃.



Figure S2b: ¹³C NMR spectrum of 1c in CDCl₃.



Figure S2c: FTIR spectrum of 1c.



Figure S3a: ¹H NMR spectrum of PDI 2a in CDCl₃.



Figure S3b: ¹³C NMR spectrum of PDI 2a in CDCl₃.



Figure S3c: FTIR spectrum of PDI 2a.







190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

150 100 50

Figure S4b: ¹³C NMR spectrum of PDI 2b in CDCl₃.



Figure S4c: FTIR spectrum of PDI 2b.



Figure S4d: Mass spectrum of PDI 2b.



Figure S5a: ¹H NMR spectrum of PDI 2c in CDCl₃.



Figure S5b: ¹³C NMR spectrum of PDI 2c in CDCl₃.



Figure S5c: DEPT-135 spectrum of PDI 2c in CDCl₃.



Figure S5d: ¹H-¹H COSEY NMR spectrum of PDI 2c in CDCl₃.



Figure S5e: FTIR spectrum of PDI 2c.



Figure S5f: Mass spectrum of PDI 2c.



Figure S6a: ¹H NMR spectrum of PDI 3a in CDCl₃.



Figure S6b: ¹³C NMR spectrum of PDI 3a in CDCl₃.



Figure S6c: DEPT-135 spectrum of PDI 3a in CDCl₃.



Figure S6d: ¹H–¹H COSEY NMR spectrum of PDI 3a in CDCl₃.



Figure S6e: FTIR spectrum of PDI 3a.



Figure S6f: Mass spectrum of PDI 3a.



Figure S7a: ¹H NMR spectrum of PDI 3b in CDCl₃.



Figure S7b: ¹³C NMR spectrum of PDI 3b in CDCl₃.



Figure S7c: DEPT-135 spectrum of PDI 3b in CDCl₃.



Figure S7d: FTIR spectrum of PDI 3b.



Figure S7e: Mass spectrum of PDI 3b.





Figure S8b: ¹³C NMR spectrum of PDI 3c in CDCl₃.



Figure S8c: DEPT-135 spectrum of PDI 3c in CDCl₃.



Figure S8d: ¹H-¹H COSEY NMR spectrum of PDI 3c in CDCl₃.



Figure S8e: FTIR spectrum of PDI 3c.



Figure S8f: Mass spectrum of PDI 3c.



2. Optical data of PDI 2a-2d and PDI 3a-3d

Figure S9: UV–Vis spectra of (a) PDI 2a-2c (10 μ M); (b) PDI 3a-3c (10 μ M) in different polarity solvents.



Figure S10: Fluorescence spectra of (a) **PDI 2a–2c** (10 μ M); (b) **PDI 3a–3c** (10 μ M) recorded in different polarity solvents; $\lambda_{ex} = 490$ nm, slit width (ex/em) =5/5.



Figure S11a: Plot between degree of aggregation (α) and ΔG and volume % of water for PDI 3a.



Figure S11b: Plot between degree of aggregation (α) and ΔG and volume % of water for PDI 3b.



Figure S11c: Plot between degree of aggregation (α) and ΔG and volume % of water for PDI 3c.



Figure S11d: Images of PDI 3a-3c in DMSO (as monomer state) under (a) ambient light and (b) 365 nm UV lamp.

Vol% Water	PDI 3a	PDI 3b	PDI 3c
0	1.438272	1.42807	1.412903
10	1.4375	1.417857	1.384365
20	1.39441	1.245283	1.361624
30	1.247839	0.88172	1.178947
40	1.102639	0.793478	0.859551
50	1.022556	0.751295	0.757576
60	1.039867	0.731844	0.722826
70	0.97992	0.732558	0.72619
80	0.895833	0.729412	0.713483
90	0.837963	0.735294	0.729885
99	0.74359	0.736842	0.753247

Table S1: Franck-Codon ratio of PDI 3a-3c derivatives.

Table S2: Fluorescence quantum yield of PDI 3a-3c derivatives in different water ratios.

Vol% Water	PDI 3a	PDI 3b	PDI 3c
DMSO	49.7	57.1	65
30	45.4	22.4	53.9
50	23.2	3.7	8.0
70	23.5	3.3	4.5
90	10.3	3.16	3.8
99	3.0	2.7	3.1



Figure S12. The UV–vis and fluorescence spectra of (i,ii) PDI **3c** derivatives showing aggregation behaviour in different H₂O: DMSO ratios. $\lambda_{ex} = 490$ nm, slit width (ex/em) =5/5.



Figure S13: The UV–vis and fluorescence spectra of (a,b) PDI **2a** (10 μ M) respectively showing aggregation behaviour in different DMSO-water ratios. $\lambda_{ex} = 490$ nm, slit width (ex/em) =5/5.



Figure S14: The UV–vis and fluorescence spectra of (e,f) PDI **2b** and (g,h) PDI **2c** (10 μ M) respectively showing aggregation behaviour in different DMSO-water ratios. $\lambda_{ex} = 490$ nm, slit width (ex/em) =5/5.

Vol% Water	PDI 2a	PDI 2b	PDI 2c
0	1.425743	1.449704	1.423729
10	1.423554	1.443114	1.423729
20	1.390805	1.125	1.406716
30	0.912458	0.803738	1.010989
40	0.872881	0.801887	0.798883
50	0.785714	0.661017	0.786885
60	0.783505	0.666667	0.787709
70	0.785047	0.75	0.779487
80	0.785924	0.759259	0.774359
90	0.786982	0.788991	0.790816

Table S3: Franck-Codon ratio of PDI 2a-2c derivatives.



Figure S15: Extracted Height profile of PDI 3a (1 μ M).



Figure S16: Extracted Height profile of PDI 3b (1 μ M).



Figure S17: Extracted Height profile of PDI 3c (1 µM).

Spectral Characteristics	PDI 2a	PDI 2b	PDI 2c	PDI 3a	PDI 3b	PDI 3c
Absorbance λ_{max} [nm]	535	535	535	535	537	536
Fluorescence λ_{max} [nm]	571	571	573	574	572	572
ε (molar absorptivity) [M ⁻¹ cm ⁻¹]	44700	37700	69500	53500	53700	53600
Stoke Shift (in nm)	36	36	38	39	35	36
Quantum Yield (Φ in %) in DMSO	53.82	77.71	70.52	49.74	57.12	65.11
Franck-Condon Ratio (A ₀₋₀ /A ₀₋₁)	1.42	1.44	1.42	1.43	1.43	1.41
Specific optical rotation ($[\alpha]_D^{25}$)	+32.5	+15.0	+40	-90	-125	-60
HOMO Calculated from DFT (eV)	-5.832	-5.825	-5.809	-7.869	-7.878	-7.885
LUMO calculated from DFT (eV)	-3.421	-3.416	-3.418	-5.541	-5.551	-5.556
Energy gap (Eg) from DFT (eV)	2.41	2.41	2.39	2.33	2.33	2.33
HOMO calculated from CV (eV)	-5.479	-5.445	-5.559	-7.376	-7.414	-7.503
LUMO calculated from CV (eV)	-3.531	-3.602	-3.647	-5.356	-5.366	-5.31
Energy gap (Eg) from CV (eV)	1.95	1.84	1.91	2.02	2.05	2.19
λ_{ex} [nm] calculated from (TD DFT)	528.65	528.91	528.61	543.35	543.79	543.86
Angle of Twist (°)	1.48, 1.07	0.64,	1.50,	-0.79, -	-0.52,	1.54,
		1.06	2.43	0.07	2.00	1.55

Table S4. Spectral and photophysical characteristics of PDI 2a–2d and PDI 3a–3d.



Figure S18. HOMO-LUMO molecular orbital analysis, B3LYP/6-31G* energy optimized structure and cyclic voltammograms (CV) of PDI **3c**. CV was recorded in CH_2Cl_2 solutions containing 0.1 M TBAP as supporting electrolyte with Scan rate of 50 mV s⁻¹.

3. TGA data of synthesized derivatives



Figure S19: TGA Data of 1a-1c derivatives.



Figure S20: TGA Data of PDI 2a-2c derivatives.



Figure S21: TGA Data of PDI 3a-3c derivatives.

4. Specific Optical Rotation data of 1d, PDI 2a-2c and PDI 3a-3c

Sample Code - PDI 1a

Anton Paar Polarimeter - Measurement(s)

MCP 150 Software Version: 1.50.4074.82 Serial Number: 82104498

Unique Id 529

- Sample Name: > Date:
- Username:
- Sample State:

PR 83 A 10/31/2020 - 10:34 AM Administrator Ok

Specific Rotation

+10.000 *

- Measurement Mode:
- Measurement Result:
- Concentration: Optical Rotation:
- Set Temperature:
- Temperature:

+0.400 g/100ml +0.004 * +25.0 °C +25.0 °C

Sample Code - PDI 1b

Anton Paar Polarimeter - Measurement(s) MCP 150

Software Version: 1.50.4074.82 Serial Number: 82104498

Unique Id 530

- Sample Name:
 Date:
 Username:
- Sample State:

PR81 A 10/31/2020 - 10:42 AM Administrator Ok

Specific Rotation

- Measurement Mode:
- Measurement Result:
- Concentration:
- Optical Rotation:
- Set Temperature:
 Temperature:
- +0.400 g/100ml +0.006 ° +25.0 °C +25.0 °C

+15.000 °

Sample Code - PDI 1c

Anton Paar Polarimeter - Measurement(s)

MCP 150 Software Version: 1.50.4074.82 Serial Number: 82104498

Unique Id 549

Sample Name:	PR 36
Date:	10/31/2020 - 01:42 PM
Username:	Administrator
Sample State:	Ok
Measurement Mode:	Specific Rotation
Measurement Result:	-5.000 °
Concentration:	+0.400 g/100ml
Optical Rotation:	0.000 *
Set Temperature:	+25.0 °C
Temperature:	+25.0 °C

Figure S22: Specific optical rotation of 1a-1c derivatives.

Sample Code - PDI 2a

Anton Paar Polarimeter - Measurement(s)

Administrator Ok

+25.0 °C +25.0 °C

Specific Rotation +32.500 * +0.400 g/100ml +0.013 *

Pr 83 B 10/31/2020 - 11:20 AM

MCP 150 Software Version: 1.50.4074.82 Serial Number: 82104498

Unique Id 538

- Sample Name:
 Date:
- Usemame:
- Sample State:
- Measurement Mode:
 Measurement Result:
 Concentration:
 Optical Rotation:
 Set Temperature:
 Temperature:

Sample Code - PDI 2b

Anton Paar Polarimeter - Measurement(s) MCP 150 Software Version: 1.50.4074.82 Serial Number: 82104498

Unique Id 417

- Sample Name:
 Date: b 03/12/2020 - 05:45 PM
- Username:
 Sample State: Administrator
 - asurement Mode: Specific Rota +15.000 * ation
- Measurement Result:
 Concentration:
 Optical Rotation: +0.400 g/100ml +0.006 *
- +25.0 °C Set Temperature: Temperature: +25.0 °C

Sample Code - PDI 2c

Anton Paar Polarimeter - Measurement(s) MCP 150 Software Version: 1.50.4074.82 Serial Number: 82104498

Unique Id 582

Sample Name:	PR 65
Date:	01/09/20
Usemame:	Administ
Sample State:	Ok
Measurement Mode:	Specific
Measurement Result:	+40.000
Concentration:	+0.200 g
Optical Rotation:	+0.008 *
Set Temperature:	+25.0 °C
Temperature:	+25.0 °C
Wavelength in air:	+589.28
Wavelength in vacuum:	+589.44
Cell Length:	+10.00 m

Figure S23: Specific optical rotation of PDI 2a-2c derivatives.

- 21 12:00 PM
- Rotation /100ml

- nm
- - nm

 - +10.00 m







Figure S25: MTT assay of PDI 3a-c.



Figure S26 (a) MTT assay of PDI Br; (b) brightfield image; (c, d) fluorescence images of MG-63 cells incubated with PDI Br $(1 \mu M)$ for 30 minutes.



Figure S27: (top) Proposed ionic self-assembly of PDI **3b** with Na AOT and (bottom) ¹H NMR titration of PDI **3b** upon addition of NaAOT recorded in DMSO (d_6).