Supporting Information

Alignment and photooxidation dynamics of a perylene diimide chromophore in lipid bilayers

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Contents

S1. Synthesis and characterization of 2 and $[1]^{2+}$

Synthesis of N,N'-di(butylenedimethylamine)-3,4,9,10-perylenediimide (2)

In 20 mL of isobutanol perylene tetracarboxylic dianhydride (0.100 g, 0.255 mmol, 1.00 eq.) and (4-aminobutyl) dimethylamine (0.14 mL, 1.02 mmol, 4.00 eq.) were combined, stirred and heated at 90 °C for 24 h under argon atmosphere. After the mixture was cooled to room temperature, the crude product was collected by filtration. To remove unreacted PTCDA, to the mixture was added 5% aqueous NaOH solution and stirred at 90 °C for 30 minutes. The product was separated from solvent by filtration and washed with water and ethanol. The red solid powder then dried under vacuum to give 0.14 g (0.238 mmol, 95% yield) product.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 8.0 Hz, 4H), 8.53 (d, *J* = 8.1 Hz, 4H), 4.20 (t, 4H), 2.45 – 2.23 (m, 4H), 2.22 (s, 12H), 1.86 – 1.67 (m, 4H), 1.61 – 1.39 (m, 4H).

MALDI-MS: calcd. for $[C_{36}H_{36}N_4O_4]^+$ (m/z): 588.27, found: 588.27

Anal. calcd. for $C_{36}H_{36}N_4O_4$: C, 73.45; H, 6.16; N, 9.52; O, 10.87, found C, 73.16; H, 6.15; N, 9.49; O, 10.96.

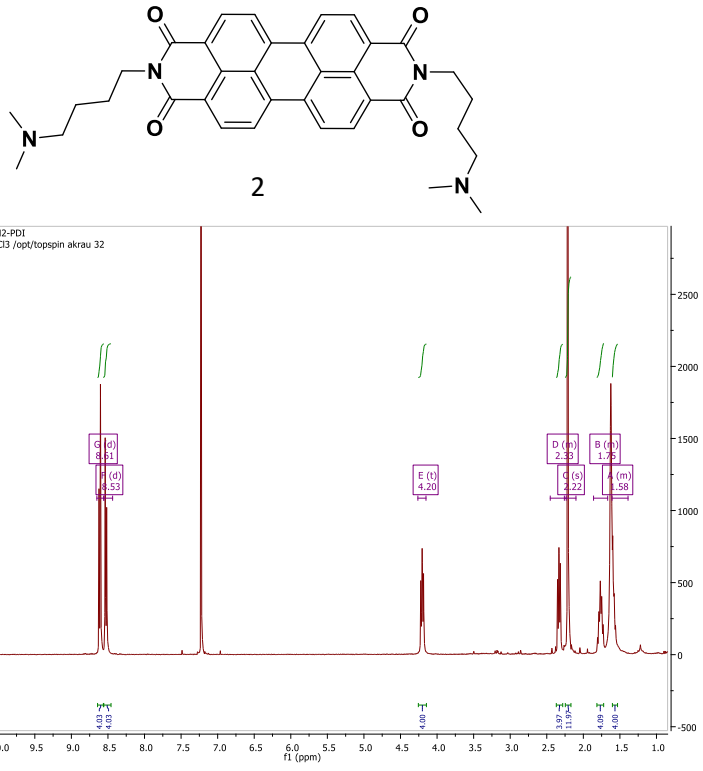


Figure S1.1: ^{1}H NMR spectrum of 2 in $CDCl_3$.

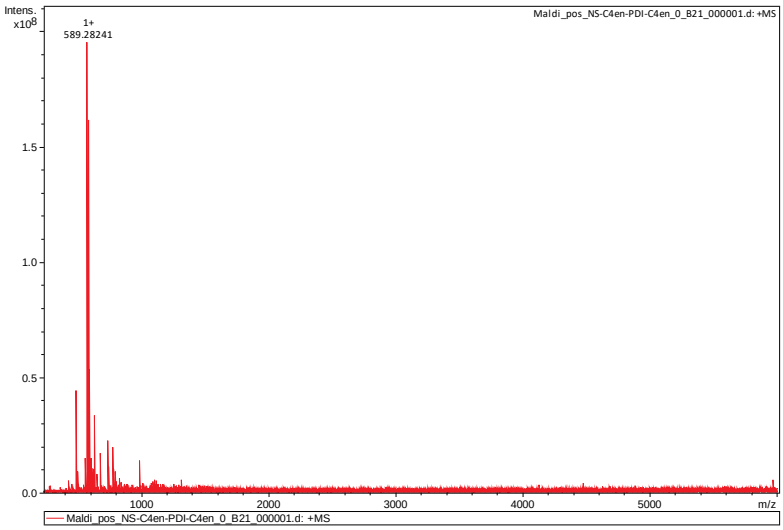


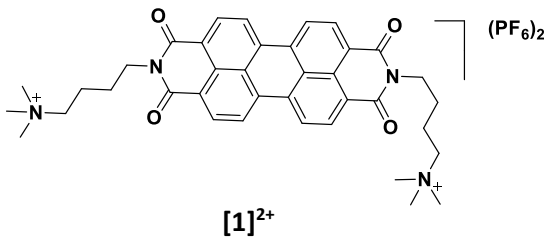
Figure S1.2: mass spectrum of 2.

Synthesis of N,N'-di(butylenetrimethylammonium)-3,4,9,10-perylenediimide $[1]^{2+}$ as PF_6 salt

A degassed solution of N,N'-di(butylenedimethylamine)-3,4,9,10-perylenediimide (0.100 g, 0.170 mmol, 1 eq.) and methyl iodide (0.287 mL, 1.70 mmol, 10 eq.) in 10 mL of toluene was refluxed for 3 h under argon atmosphere. The suspended mixture was collected by filtration, washed with ether and dried under vacuum. To the aqueous solution of the obtained compound was added dropwise to an aqueous solution of NH_4PF_6. After stirring of the solution at 65 °C for 1 h, the precipitate was centrifugated, washed with water to remove produced exchanged salts and dried under vacuum to give 0.12 g (0.130 mmol, 76 % yield) of the desired product.

^{1}H NMR (400 MHz, CD_3CN) δ 8.47 – 8.30 (m, 8H), 4.18 (t, *J* = 6.7 Hz, 4H), 3.39 – 3.29 (m, 4H), 3.04 (s, 18H), 1.85 – 1.70 (m, 8H).

MALDI-MS: calcd. for $[C_{38}H_{42}F_6N_4O_4P]^{2+}$(m/z): 763.28, found: 763.28



$[1]^{2+}$

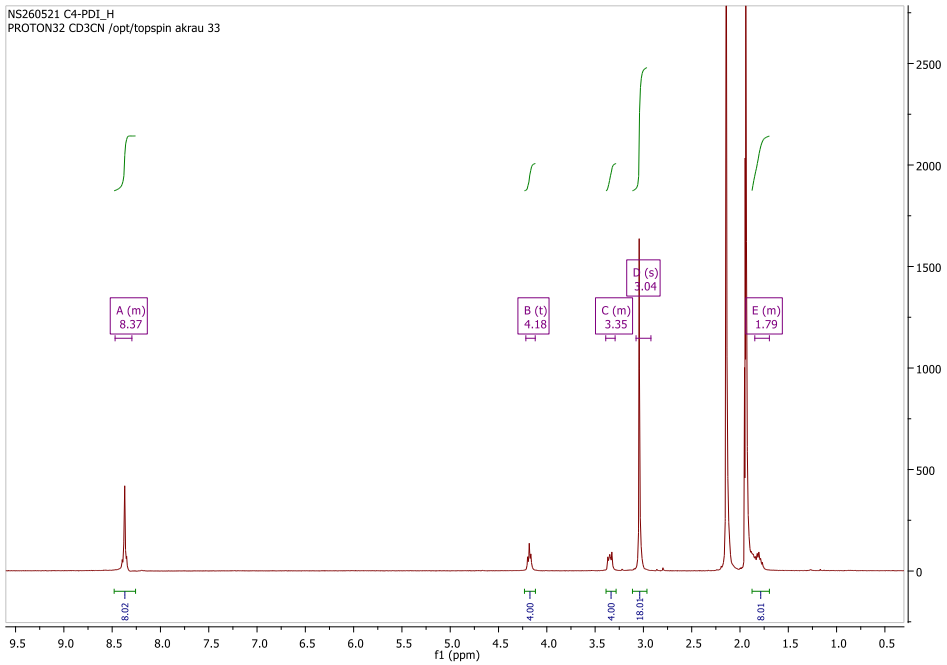


Figure S1.3: ^{1}H NMR spectrum of **[1]$^{2+}$**.

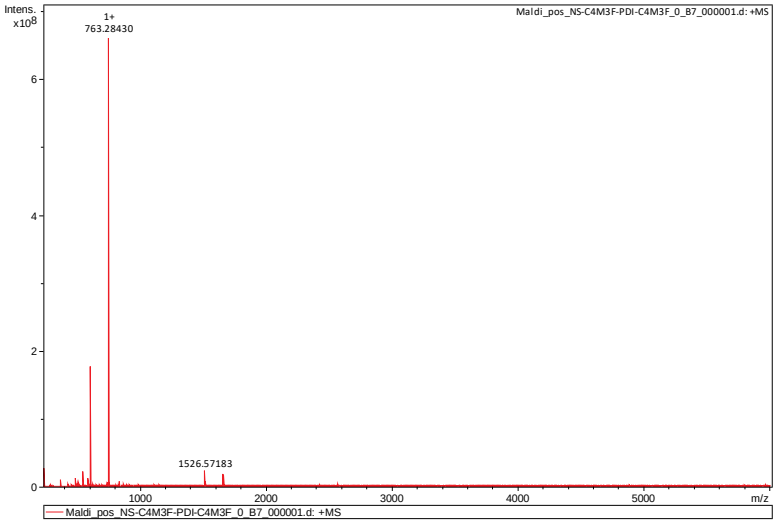


Figure S1.4: mass spectrum of **[1]$^{2+}$**.

Anal. calcd. for $C_{38}H_{42}F_{12}N_4O_4P_2 \cdot 0.1\ NH_4PF_6$: C, 49.34; H, 4.62; N, 6.21; found C, 49.53; H, 4.81; N, 6.07.

S2. Photooxidation of $[1]^{2+}$ and temporally resolved UV-vis spectra in DOPG

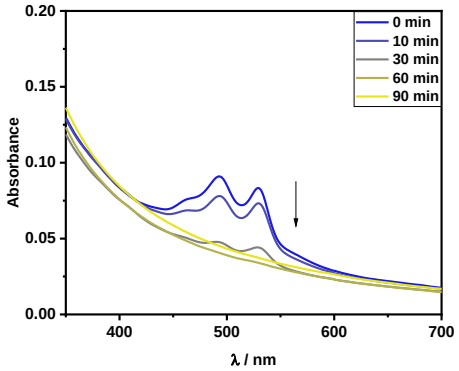


Figure S2.1. Photooxidation of **$[1]^{2+}$** and temporally resolved UV-vis spectra in DOPG:(14:0 PEG2000 PE):**$[1]^{2+}$** = 100:1:1 liposomes in phosphate buffer (10 mM, pH 7.0) without size exclusion.

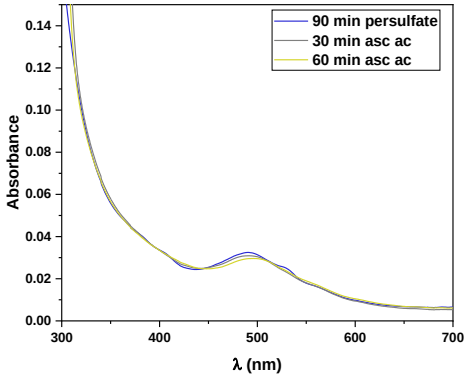


Figure S2.2. UV-vis spectra of Addition of photooxidized **$[1]^{2+}$** upon addition of 100 mM of ascorbic acid. Experimental conditions: DOPG:(14:0 PEG2000 PE):**$[1]^{2+}$** = 100:1:1 liposomes in phosphate buffer (10 mM, pH 7.0) without size exclusion with 50 mM of sodium persulfate after irradiation of 90 min and afterward additional 100 mM of ascorbic acid.

S3. Stern-Volmer quenching experiment

Solutions were prepared as described in main pages.

In cuvette:

V = 3 mL

[1]$^{2+}$ = 1 uM

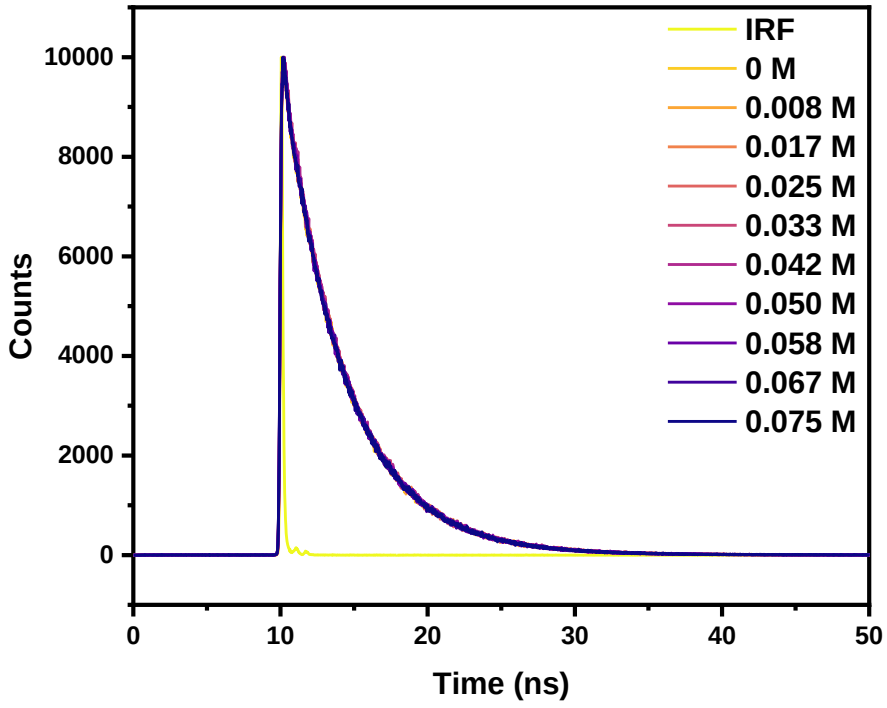


Figure S3.1. Kinetic traces of luminescence decay upon excitation at 450 nm in acetonitrile/water 1:1 (V/V) and 1 μM **[1]**$^{2+}$ and various concentrations of $Na_2S_2O_8$ as quencher.

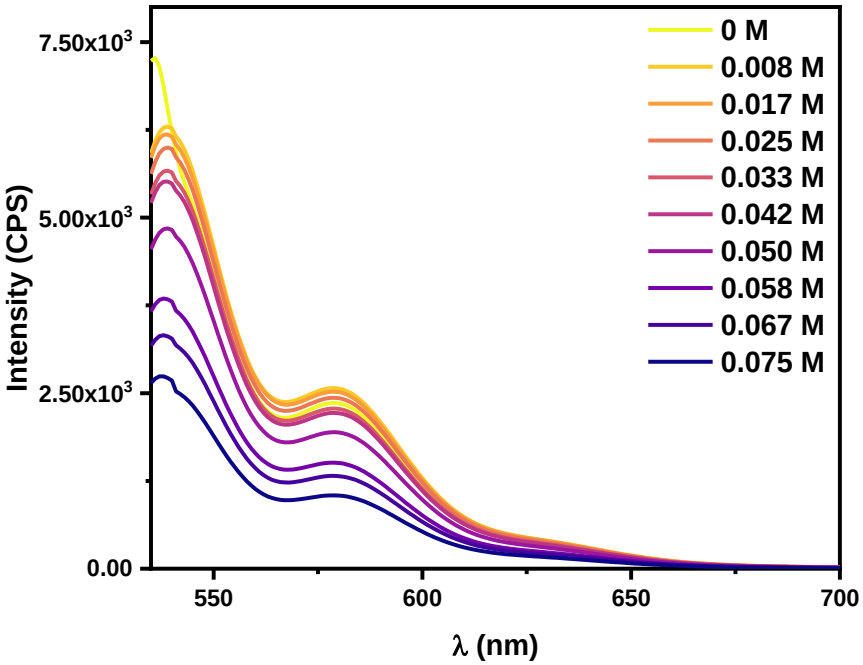


Figure S3.2. Luminescence quenching upon addition various concentrations of $Na_2S_2O_8$ in acetonitrile/water 1:1 (V/V) and 1 μM **[1]**$^{2+}$.

Liposomes were prepared as described in methods section.

In cuvette:

V = 3 mL

[1]$^{2+}$= 1.67 μM

[DOPG] = 167 μM

[14:0 PEG2000 PE] = 0.17 μM

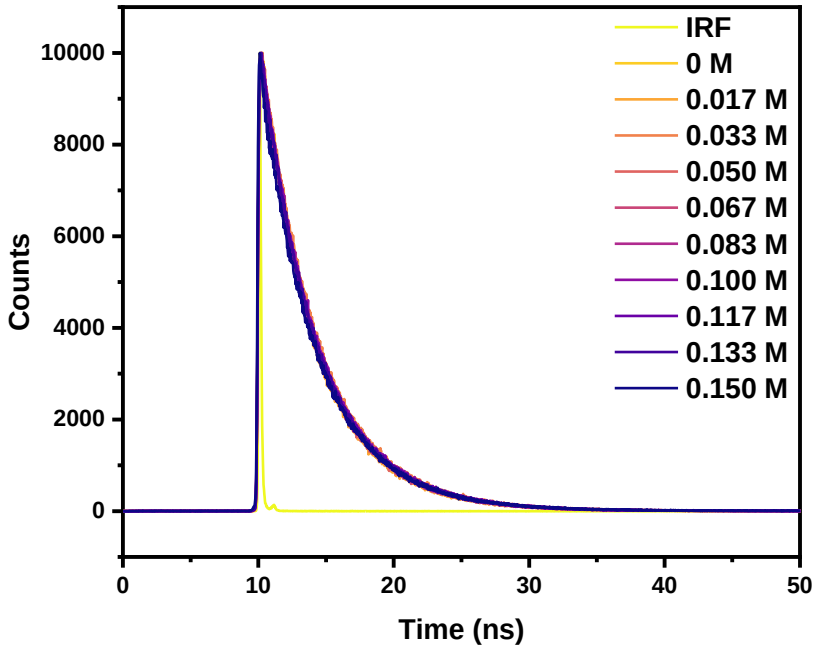


Figure S3.3. Kinetic traces of luminescence decay upon excitation at 450 nm at pH 7.0 of DOPG liposomes without size exclusion chromatography with 1% (14:0 PEG2000 PE), 1% **[1]**$^{2+}$ and various concentrations of $Na_2S_2O_8$ as quencher.

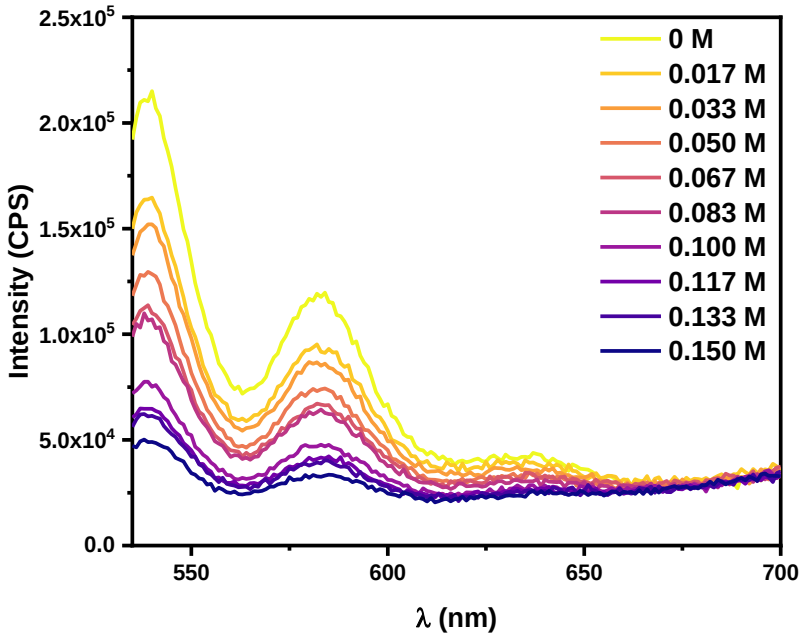


Figure S3.4. Luminescence quenching upon addition various concentrations of $Na_2S_2O_8$ in DOPG liposomes without size exclusion chromatography with 1% (14:0 PEG2000 PE), 1% **[1]**$^{2+}$.

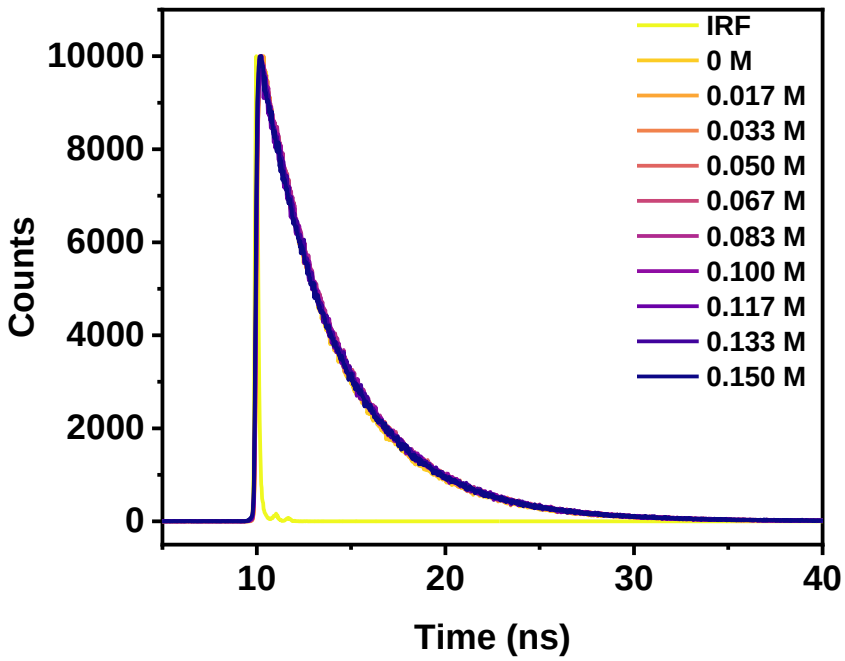


Figure S3.5. Kinetic traces of luminescence decay upon excitation at 450 nm at pH 7.0 of DOPG liposomes with size exclusion chromatography with 1% (14:0 PEG2000 PE), 1% **[1]**$^{2+}$ and various concentrations of $Na_2S_2O_8$ as quencher.

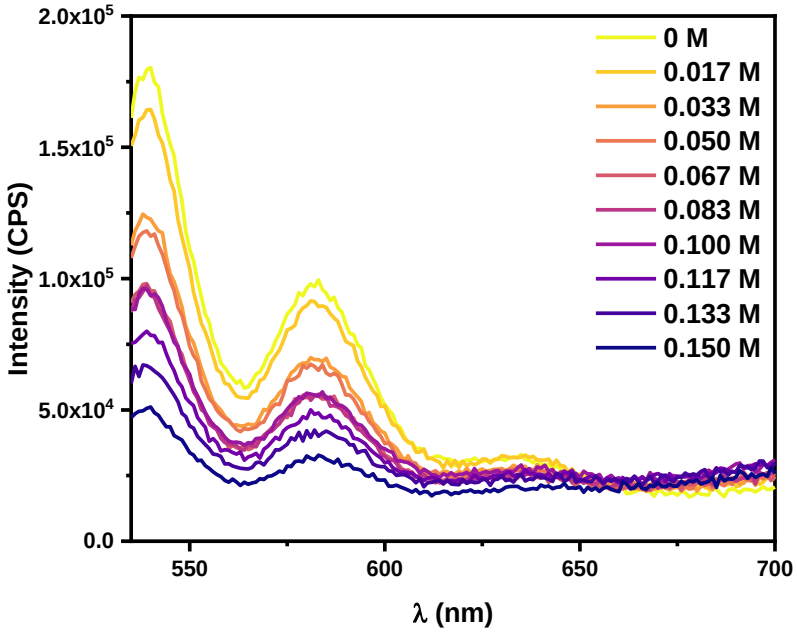


Figure S3.6. Luminescence quenching upon addition various concentrations of $Na_2S_2O_8$ in DOPG liposomes with size exclusion chromatography with 1% (14:0 PEG2000 PE), 1% **[1]**$^{2+}$.

S4. Typical hydrodynamic diameter of DOPG liposome containing $[1]^{2+}$

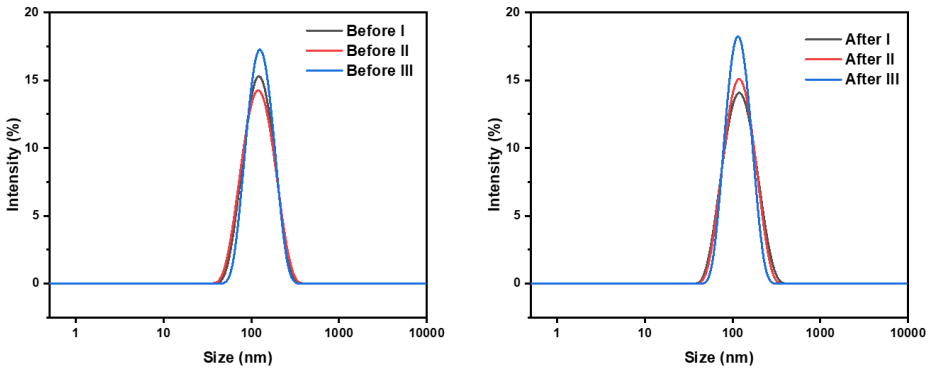


Figure S4.1. DLS measurements of DOPG liposomes with size exclusion chromatography with 1% (14:0 PEG2000 PE), 1% **$[1]^{2+}$,** before (left) and after (right) photooxidation reaction.

Table S1. DLS data: average size and polydispersity index, before and after photooxidation reaction.

Parameters	Before	After
	Mean	Mean
Z-average (nm)	117	111
Polydispersity index	0.11	0.07

S5. Coordinates of $[1]^{2+}$

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N-substituted perylene diimide

C	-2.87525	0.33453	-2.20917
C	-1.47598	0.33312	-2.22232
C	-0.73452	-0.46864	-1.34924
C	-1.43165	-1.31061	-0.42502
C	-2.86098	-1.30408	-0.41931
C	-3.57197	-0.46982	-1.31791
C	0.73451	-0.46862	-1.34924
C	-0.73462	-2.15708	0.49533
C	0.73464	-2.15708	0.49532
C	1.43166	-1.31061	-0.42504
C	1.47747	-2.95501	1.37056

C	-1.47744	-2.95499	1.37060
C	-2.87715	-2.94018	1.37093
C	-3.57316	-2.12443	0.49022
H	-3.43712	-3.56719	2.06556
H	-3.43370	0.96855	-2.89845
C	1.47596	0.33316	-2.22231
C	2.87523	0.33458	-2.20917
C	3.57196	-0.46978	-1.31792
C	2.86099	-1.30406	-0.41934
H	3.43368	0.96862	-2.89844
C	2.87718	-2.94020	1.37088
H	3.43716	-3.56722	2.06548
C	3.57318	-2.12442	0.49017
H	-0.97164	0.98102	-2.93676
H	0.97162	0.98107	-2.93673
H	0.97373	-3.60899	2.08003
H	-0.97368	-3.60896	2.08008
C	-5.04956	-0.43312	-1.30725
C	-5.05192	-2.11493	0.51782
N	-5.69935	-1.25468	-0.38311
O	-5.69000	0.31268	-2.03849
O	-5.70382	-2.80106	1.28843
C	5.04955	-0.43307	-1.30728
C	5.05195	-2.11492	0.51775
N	5.69936	-1.25465	-0.38317
O	5.68999	0.31274	-2.03851
O	5.70385	-2.80107	1.28834
C	7.17126	-1.23607	-0.34782
H	7.49511	-2.26562	-0.15655
H	7.50873	-0.93520	-1.34588
C	7.77571	-0.31772	0.71914

H	8.86068	-0.50404	0.70476
H	7.42635	-0.63122	1.71627
C	7.54817	1.19116	0.51366
H	8.35409	1.74123	1.02110
H	7.62013	1.41482	-0.55943
C	6.20222	1.63437	1.07170
H	6.18316	1.52365	2.16409
H	5.38163	1.03334	0.67076
C	4.40618	3.26992	1.28716
C	6.71981	4.02413	1.51548
C	5.84735	3.37232	-0.68138
N	5.81032	3.07731	0.79141
C	-7.17125	-1.23611	-0.34775
H	-7.49509	-2.26566	-0.15645
H	-7.50873	-0.93526	-1.34581
C	-7.77569	-0.31774	0.71921
H	-8.86066	-0.50407	0.70485
H	-7.42630	-0.63121	1.71633
C	-7.54817	1.19114	0.51368
H	-8.35408	1.74122	1.02113
H	-7.62017	1.41477	-0.55941
C	-6.20221	1.63439	1.07167
H	-6.18312	1.52370	2.16406
H	-5.38162	1.03336	0.67072
C	-6.71983	4.02415	1.51539
C	-4.40620	3.26999	1.28702
C	-5.84743	3.37229	-0.68148
N	-5.81034	3.07733	0.79132
H	3.73695	2.62275	0.70905
H	4.12458	4.31999	1.15234
H	4.36511	3.00154	2.34872

H	7.74546	3.88133	1.16150
H	6.65893	3.82105	2.59060
H	6.39493	5.04953	1.30641
H	6.88824	3.40953	-1.01599
H	5.37154	4.34450	-0.85021
H	5.31473	2.57963	-1.21833
H	-6.39497	5.04955	1.30629
H	-6.65892	3.82110	2.59052
H	-7.74549	3.88133	1.16144
H	-4.36509	3.00163	2.34859
H	-4.12463	4.32006	1.15217
H	-3.73697	2.62281	0.70891
H	-5.31481	2.57960	-1.21841
H	-5.37164	4.34448	-0.85035
H	-6.88832	3.40948	-1.01606

References

[1] B. Limburg, E. Bouwman, S. Bonnet, *Chem. Commun* **2015**, *51*, 17128.