Supporting information

"Unusual fluorescence behavior of pyrene-amine containing dendrimers"

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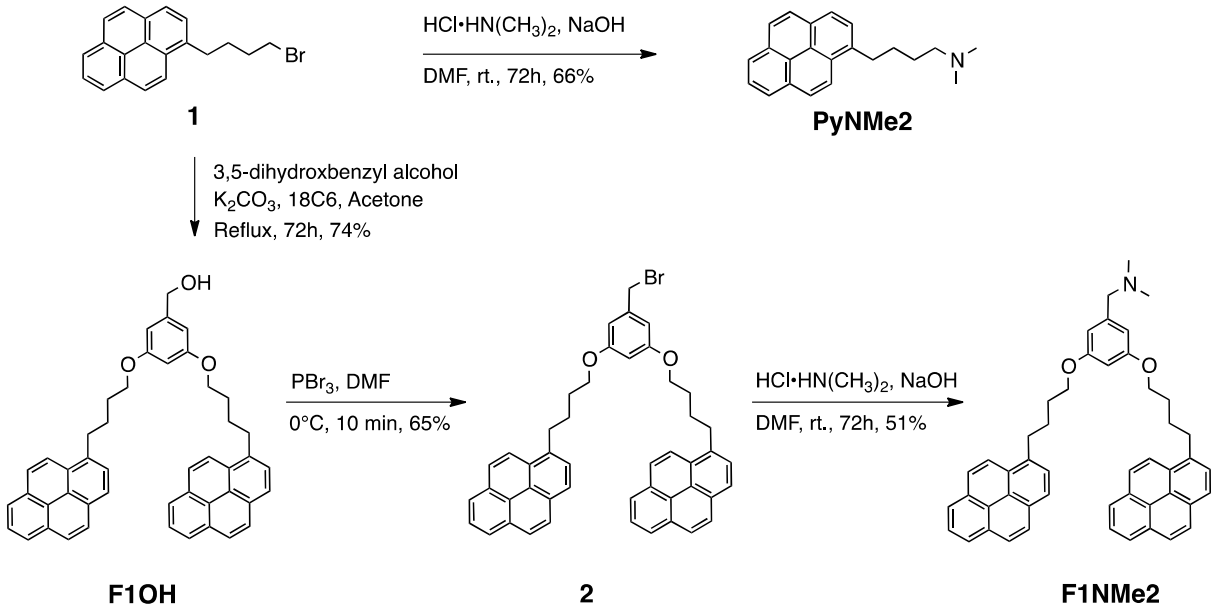
Synthetic Procedures



Scheme S1: Synthetic scheme for the model compounds **PyNMe2** and **F1NMe2**.

1-(4-Bromobutyl)pyrene (**1**)

Compound **1** was synthesized as previously reported[1]. The product was obtained as a white solid (2.190 g, 90%). ^{1}H NMR (δ ppm, 300 MHz, $CDCl_3$): 8.27-7.86 (m, 9H, CH Ar_{py}), 3.44 (t, 2H, ^{3}J = 6.3, CH_2), 3.38 (t, 2H, ^{3}J = 7.2, CH_2), 2.13-1.94 (m, 4H, CH_2).

N,N-dimethyl 4(pyren-1-yl)butan-1-amine (**PyNMe2**)

A solution of 1-(4-Bromobutyl)pyrene **1** (84 mg, 0.25 mmol) in DMF (3 ml) was prepared. Dimethylamine hydrochlorid (204 mg, 2.5 mmol) and sodium hydroxyde (100 mg, 2.5 mmol) were added to the reaction mixture and it was stirred at room temperature for 48h. Another portion of dimethylamine hydrochloride (102 mg, 1.25 mmol) was added and the reaction was reacted further for 24h at room temperature. The reaction mixture was evaporated and the crude

product was taken in dichloromethane and washed with water. The organic phase was dried over $MgSO_4$ and evaporated. The product was purified by column chromatography (dichloromethane:hexane 1:1 ; dichloromethane ; dichloromethane:methanol 97:3) to give the desired product **PyNMe2** as a light brown sticky solid (50 mg, 66 %).

^{1}H NMR (ppm, 400 MHz, $CDCl_3$): 8.26 (d, 1H, ^3J = 9.3, pyrene), 8.18-8.09 (m, 4H, pyrene), 8.02-7.97 (m, 3H, pyrene), 7.86 (d, 1H, ^3J = 7.8, pyrene), 3.38 (t, 2H, ^3J = 7.6, Py-CH_2), 3.42-3.38 (t, 2H, ^3J = 7.6, N-CH_2), 2.39 (s, 6H, N(CH_3)$_2$), 1.94-1.86 (m, 2H, CH_2-CH_2), 1.82-1.74 (m, 2H, CH_2-CH_2). ^{13}C NMR (ppm, 100 MHz, $CDCl_3$): 136.2 (C), 131.5 (C), 131.0 (C), 130.0 (C), 128.7 (C), 127.6 (CH), 127.44 (CH), 127.37 (CH), 126.8 (CH), 126.0 (CH), 125.2 (C), 125.1 (C), 125.0 (CH), 124.94 (CH), 124.87 (CH), 123.4 (CH), 59.0 (CH2), 44.4 (CH3), 33.3 (CH2), 29.3 (CH2), 26.4 (CH2). DART-MS: Calculated for $C_{22}H_{23}N$ 301.18, found 302.

First generation dendron (**F1OH**)

Compound **F1OH** was synthesized as previously reported [1]. The product was obtained as a white solid (0.980 g, 72%). ^{1}H NMR (δ ppm, 400 MHz, $CDCl_3$): 8.29-7.85 (m, 18H, CH Ar_{py}), 6.48 (d, 2H, ^4J = 2.1, ArH_o), 6.36 (t, 1H, ^4J = 2.1, ArH_p), 4.58 (d, 2H, ^3J = 3.8, CH_2 benzylic), 3.97 (t, 4H, ^3J = 5.8, O-CH_2), 3.39 (t, 4H, ^3J = 7.6, Py-CH_2), 2.10-1.88 (m, 8H, CH_2).

Brominated first generation dendron (**3**)

Compound **3** was synthesized according to the procedure previously reported by us [2]. The product was obtained as a white solid (144 mg). Yield: 65%. ^{1}H NMR (ppm, 400 MHz, $CDCl_3$): 8.28 (d, 2H, ^{3}J = 9.3, pyrene), 8.16-8.08 (m, 8H, pyrene), 8.02-7.95 (m, 6H, pyrene), 7.88 (d, 2H, ^{3}J = 7.8, pyrene), 6.50 (d, 2H, ^{4}J = 2.2, ArH_o), 6.36 (t, 1H, ^{4}J = 2.2, ArH_p), 4.36 (s, 2H, ArCH_2-Br), 3.98 (t, 4H, ^{3}J = 6.2, O-CH_2), 3.41 (t, 4H, ^{3}J = 7.6, Py-CH_2), 2.08-1.90 (m, 8H, CH_2-CH_2).

N,N-dimethyl first generation dendron (**F1NMe2**)

A solution of compound **3** (66 mg, 0.08 mmol) in DMF (3 ml) was prepared. Dimethylamine hydrochlorid (70 mg, 0.86 mmol) and sodium hydroxyde (34 mg, 0.86 mmol) were added to the reaction mixture and it was stirred at room temperature for 48h. Another portion of dimethylamine hydrochlorid (35 mg, 0.43 mmol) was added and the reaction was reacted further for 24h at room temperature. The reaction mixture was evaporated and the crude product was taken in dichloromethane and washed with water. The organic phase was dried over $MgSO_4$ and evaporated. The product was purified by column chromatagraphy (dichloromethane:hexane 1:1 ; dichloromethane ; dichloromethane:methanol 97:3) to give the desired product **F1NMe2** as a light brown sticky solid (30 mg, 51 %).

^{1}H NMR (ppm, 400 MHz, $CDCl_3$): 8.28 (d, 2H, ^{3}J = 9.3, pyrene), 8.16-8.07 (m, 8H, pyrene), 8.02-7.95 (m, 6H, pyrene), 7.87 (d, 2H, ^{3}J = 7.8, pyrene), 6.50 (d, 2H, ^{4}J = 1.9, ArH_o), 6.36 (t, 1H, ^{4}J = 1.9, ArH_p), 4.00 (t, 4H, ^{3}J = 6.2, O-CH_2), 3.42-3.38 (m, 6H, Py-CH_2, ArCH_2-N), 2.28 (s, 6H, N(CH_3)$_2$), 2.06-1.91 (m, 8H, CH_2-CH_2). ^{13}C NMR (ppm, 100 MHz, $CDCl_3$): 160.3 (C), 136.7 (C), 131.5 (C), 131.0 (C), 129.9 (C), 128.7 (C), 127.6 (CH), 127.4 (CH), 127.3 (CH),

126.7 (CH), 125.9 (CH), 125.2 (C), 125.1 (C), 125.0 (CH), 124.9 (CH), 124.8 (CH), 123.5 (CH), 107.7 (CH), 100.7 (CH), 67.9 (CH2), 64.3 (CH2), 45.1 (CH3), 33.3 (CH2), 29.4 (CH2), 28.4 (CH2).

Cyclen dendrimer of generation zero **(CyPy4)** first generation (**CyPy8**) and second generation (**CyPy16**) were synthesized as previously reported by us [3].

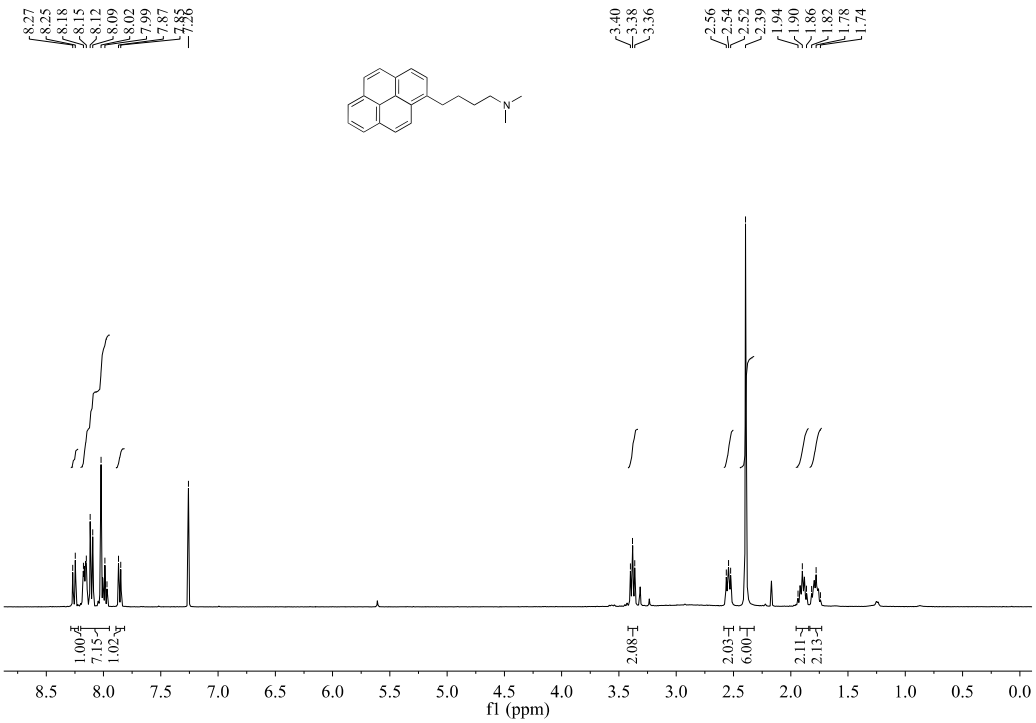


Figure S1: ^{1}H-NMR spectra of **PyNMe2**

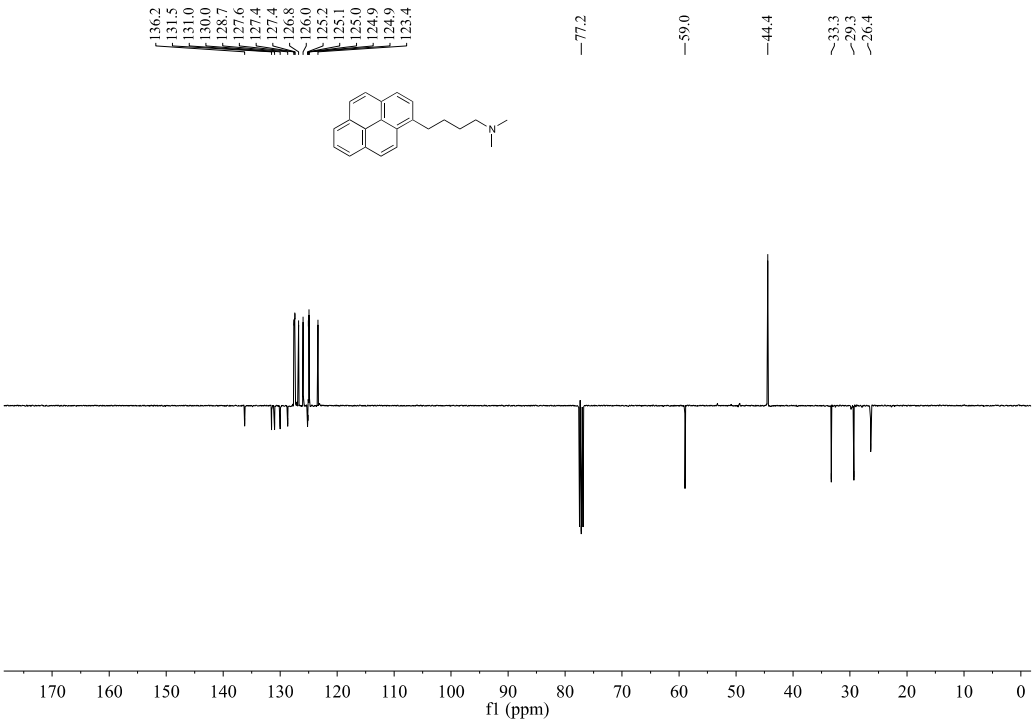


Figure S2: ^{13}C-NMR spectra of **PyNMe2**

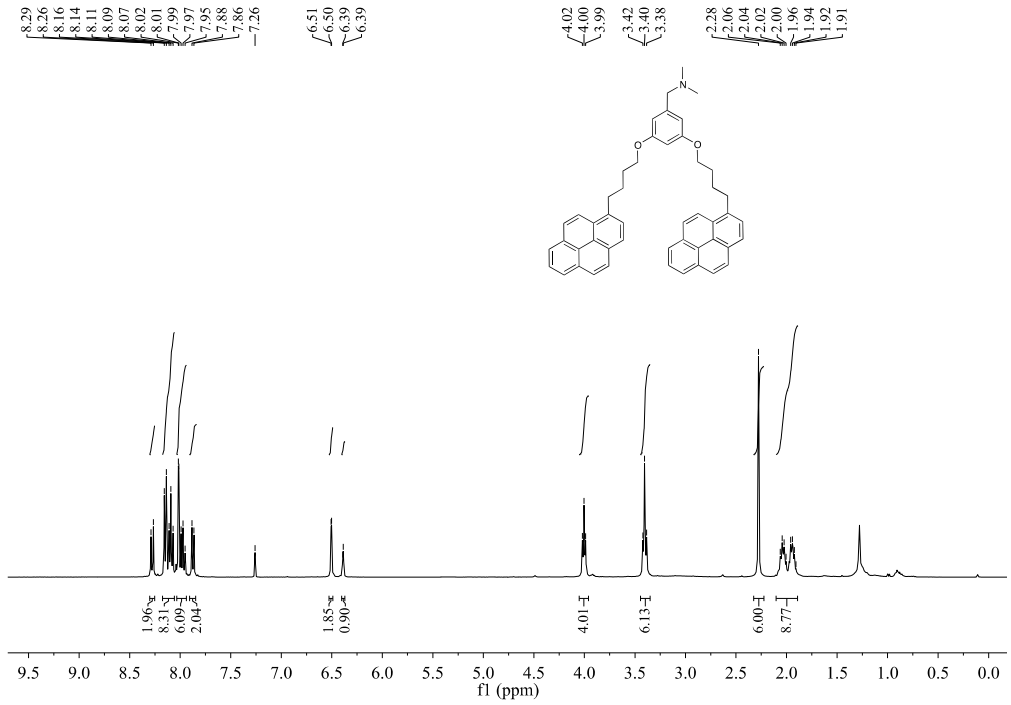


Figure S3: ^{1}H-NMR spectra of **F1NMe2**

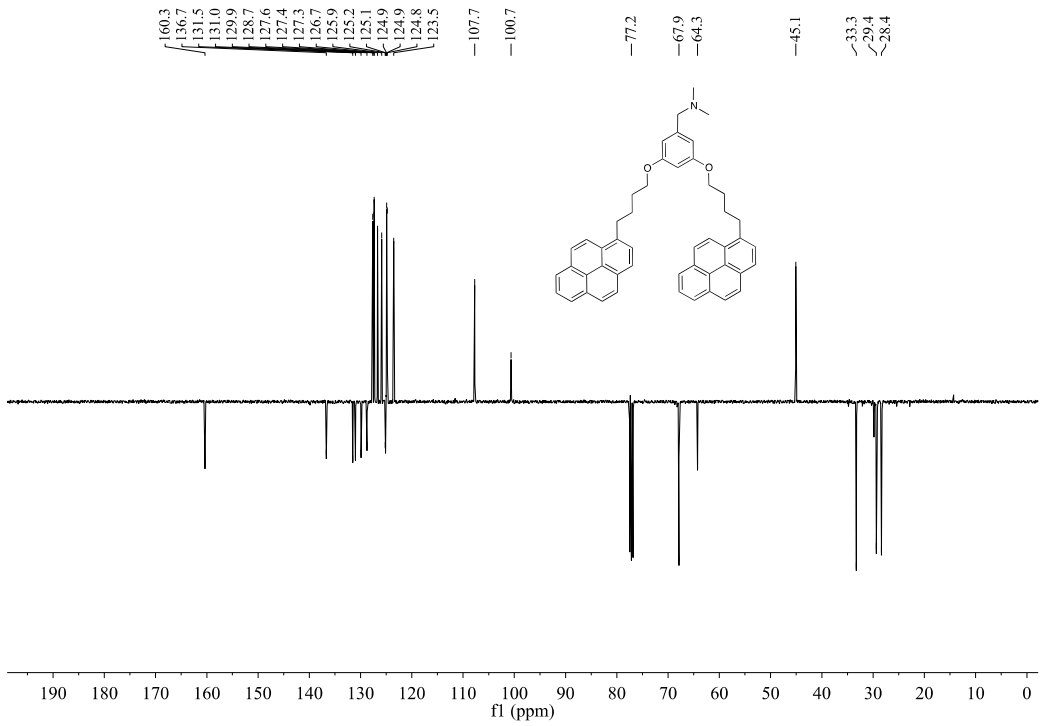


Figure S4: ^{13}C-NMR spectra of **F1NMe2**

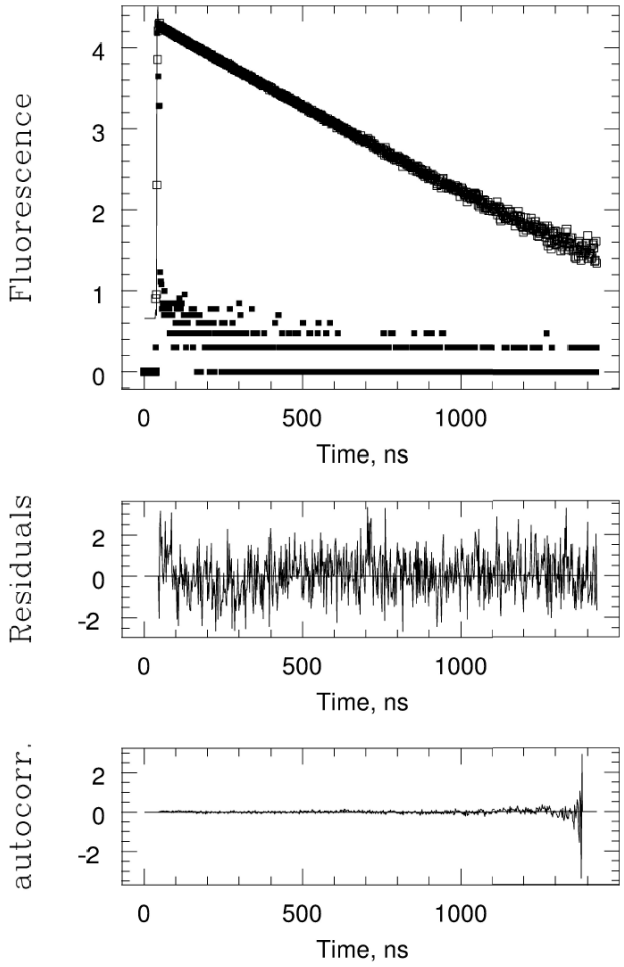
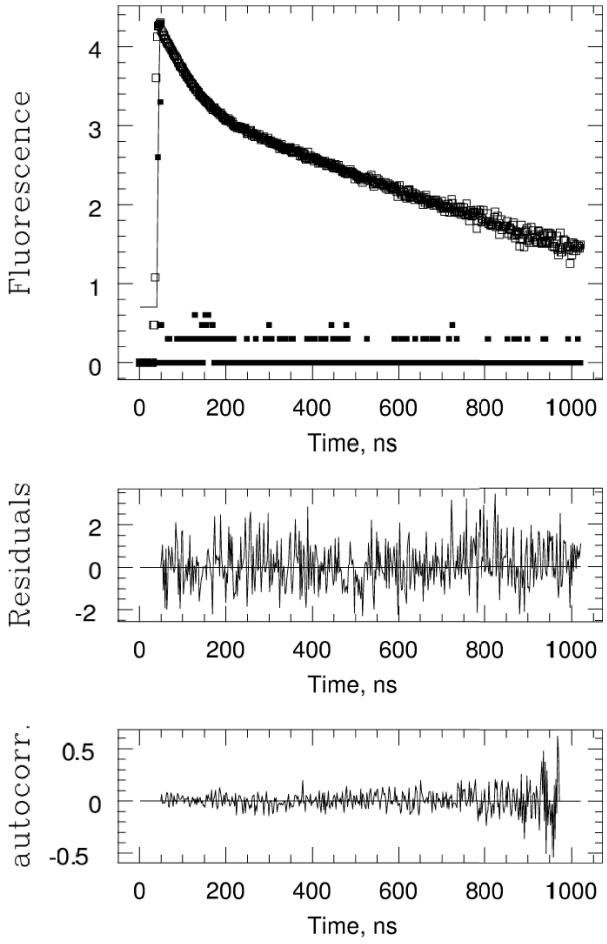


Figure S5. SPC of control compound PyOH



	a_1	τ_1	a_2	τ_2
PyNMe2	0.885	36.06	0.115	209.41

Figure S6. SPC of control compound PyNMe2

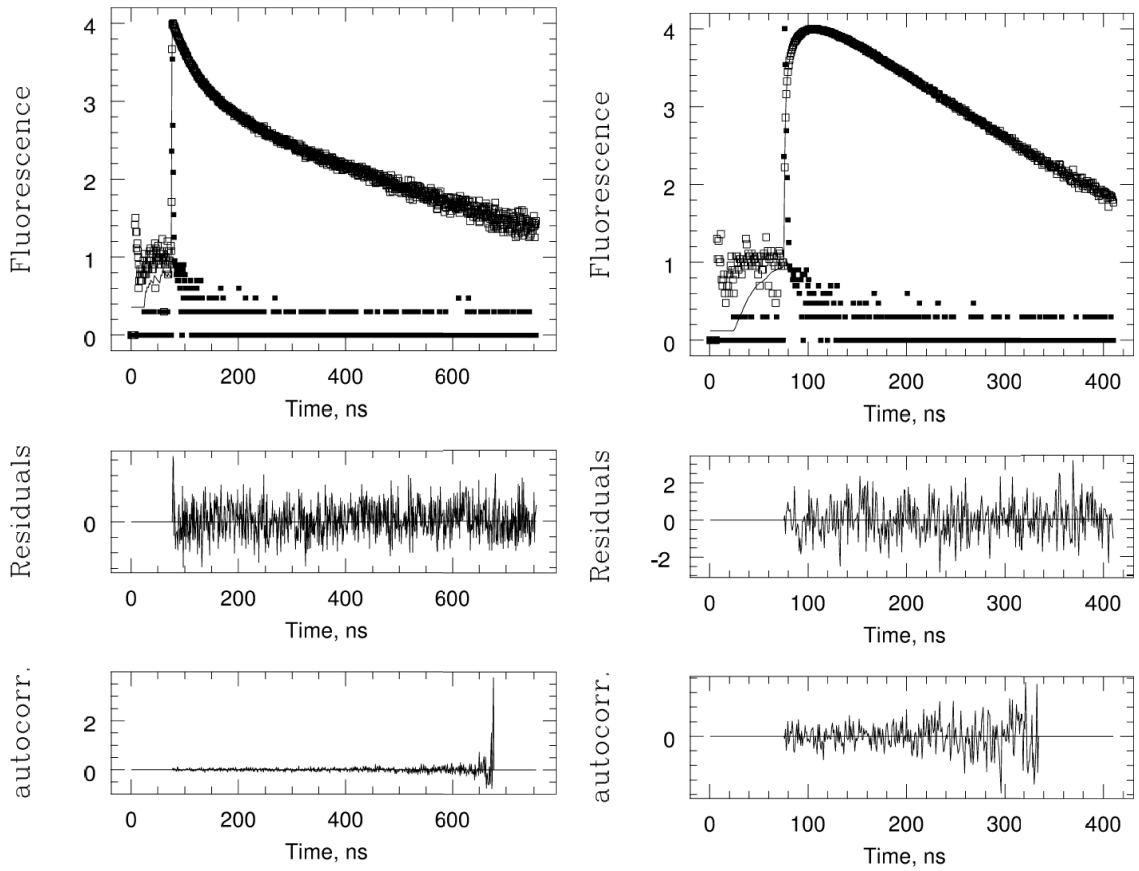


Figure S7. SPC of control compound F1OH. On the right the monomer decay and on the left the excimer decay.

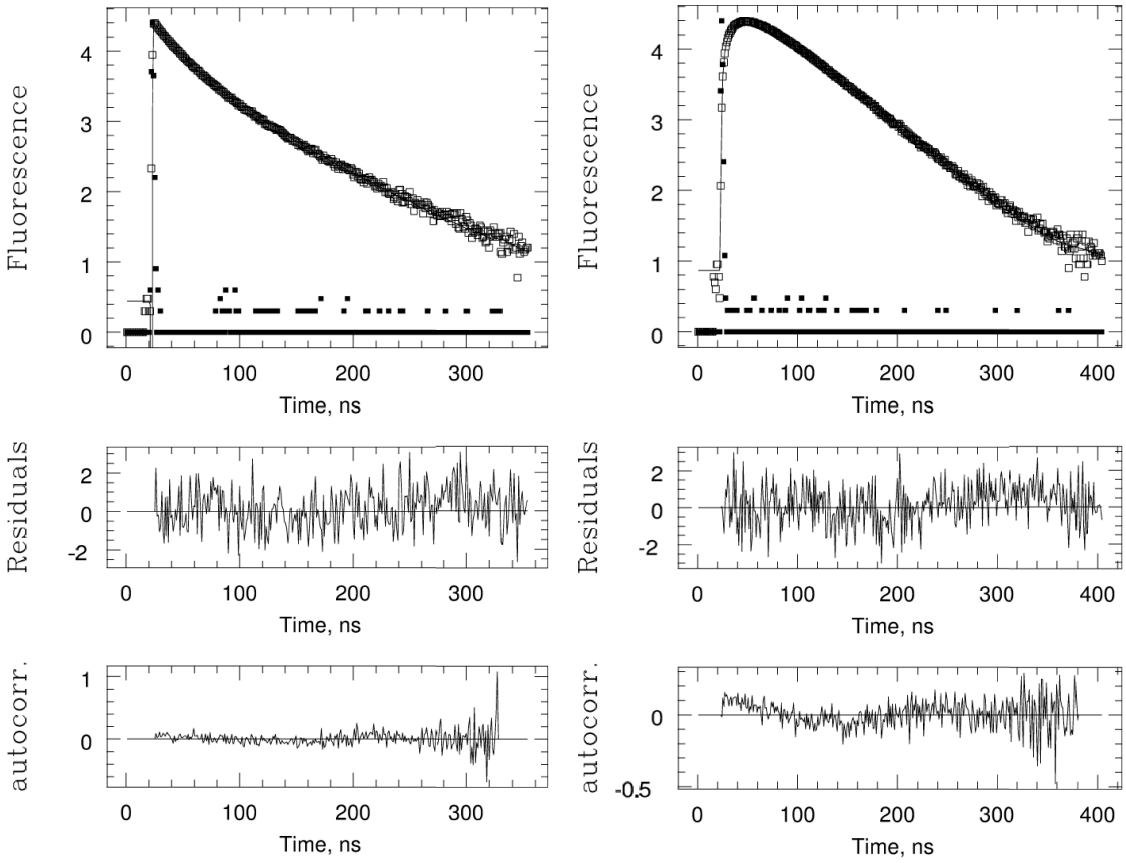


Figure S8. SPC of control compound F1NMe2. On the right the monomer decay and on the left the excimer decay.

THF analysis

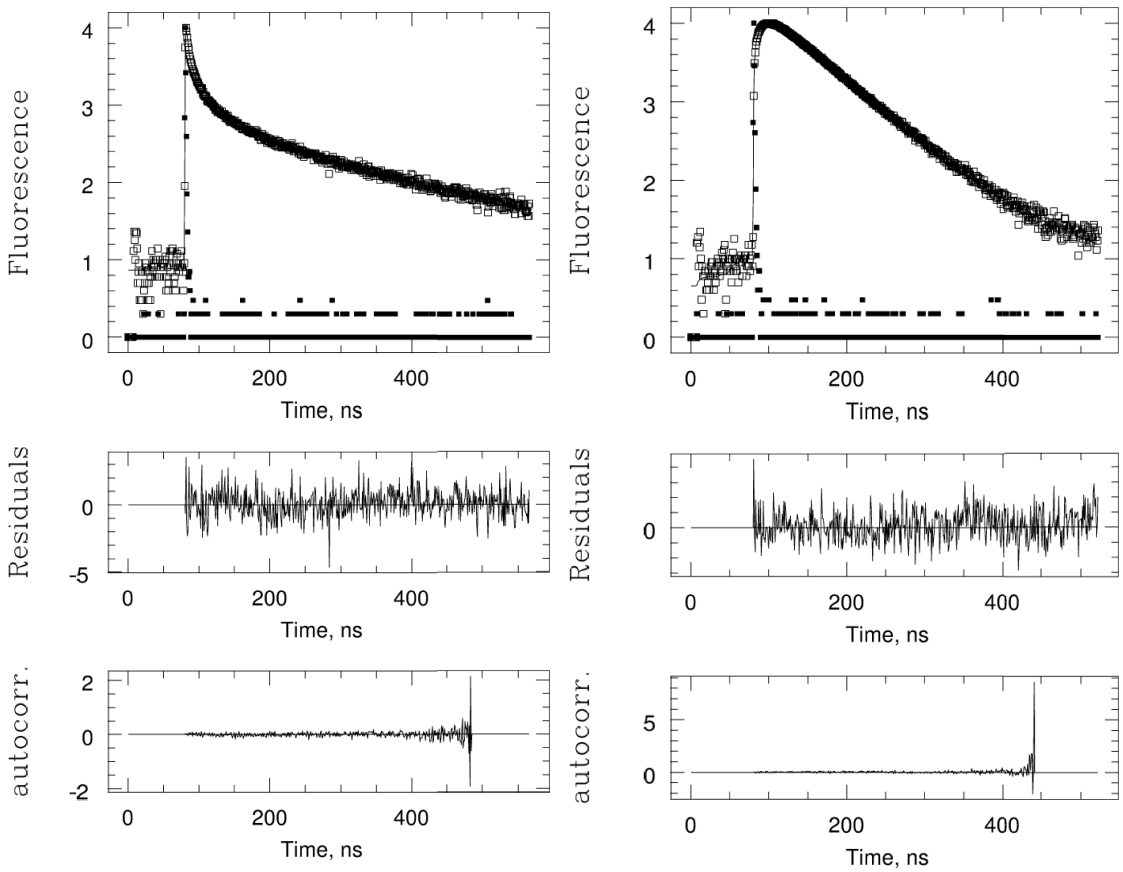


Figure S9. SPC of compound CyPy4 in THF. On the right the monomer decay and on the left the excimer decay.

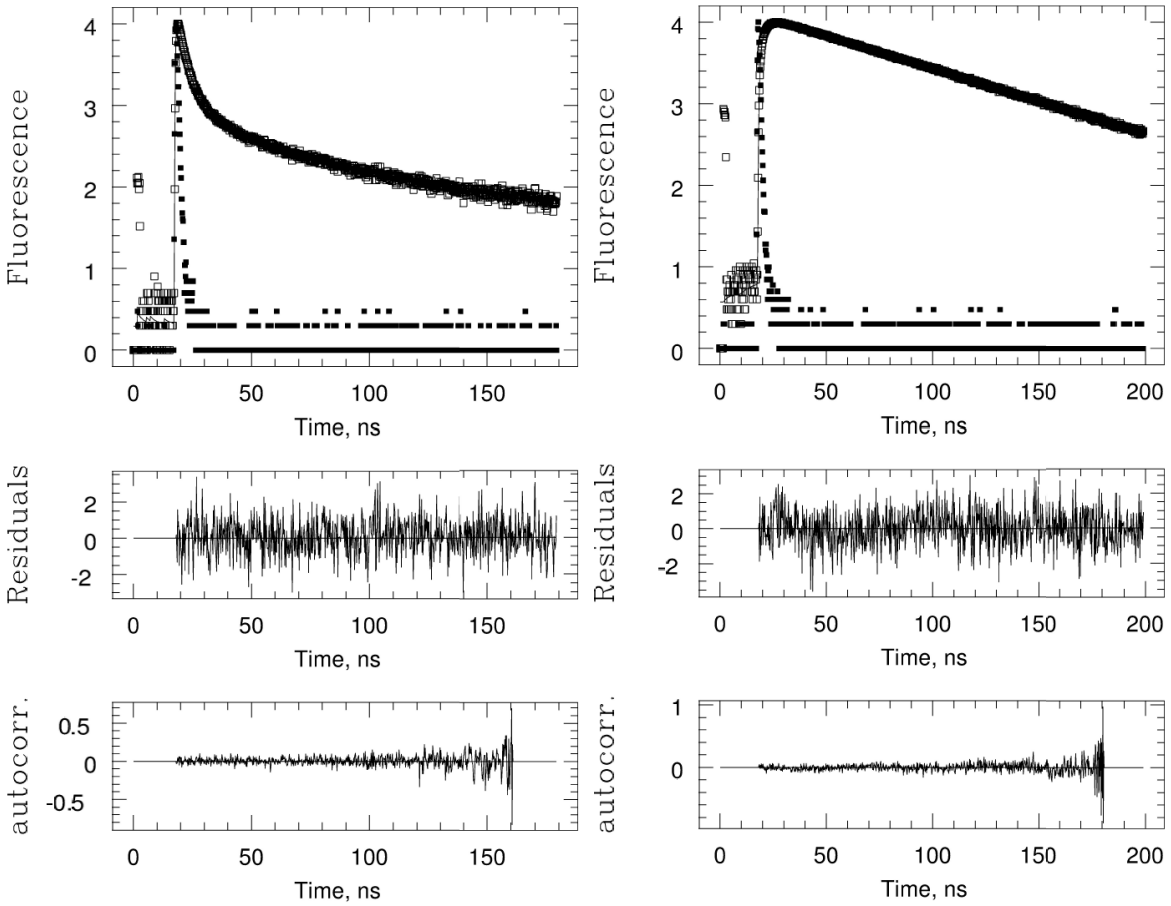


Figure S10. SPC of compound CyPy8 in THF. On the right the monomer decay and on the left the excimer decay.

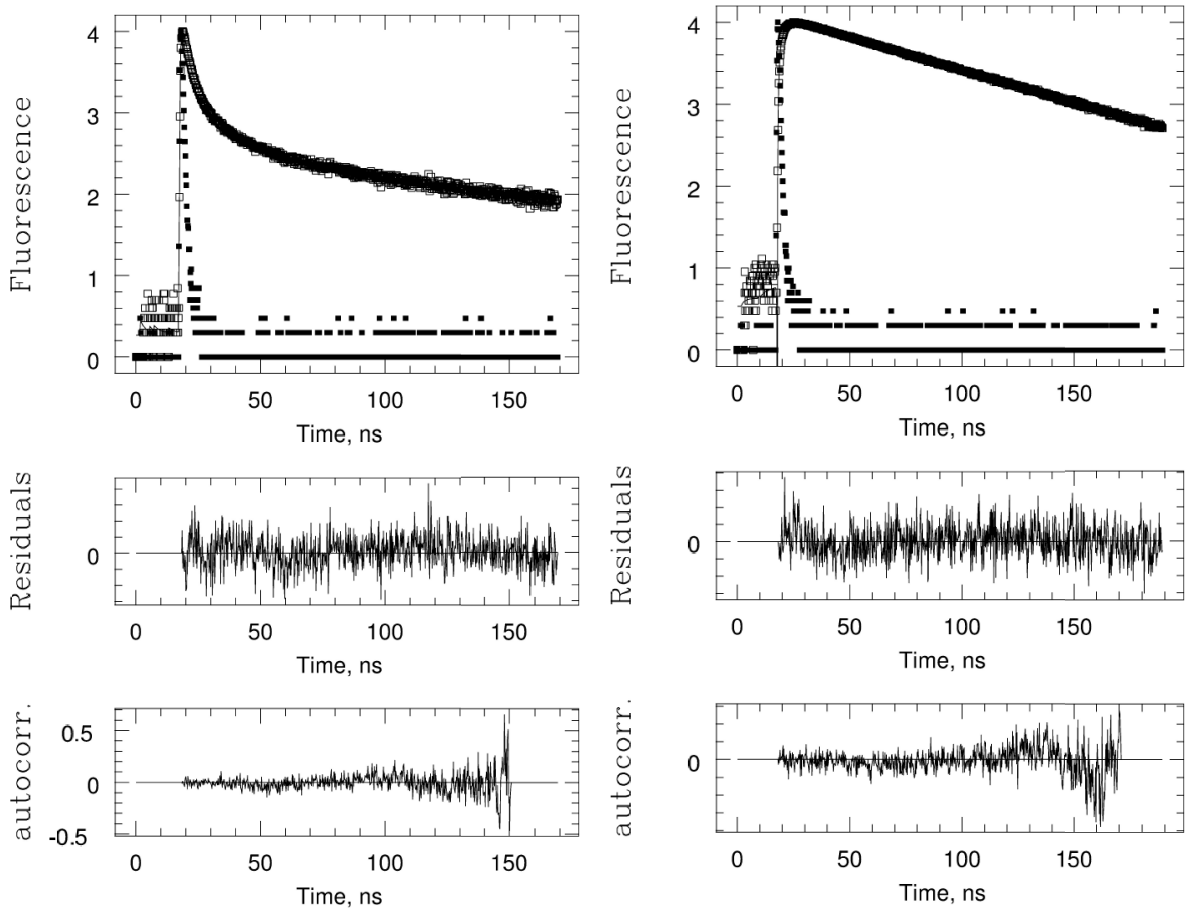


Figure S11. SPC of compound CyPy16 in THF. On the right the monomer decay and on the left the excimer decay.

DMF analysis

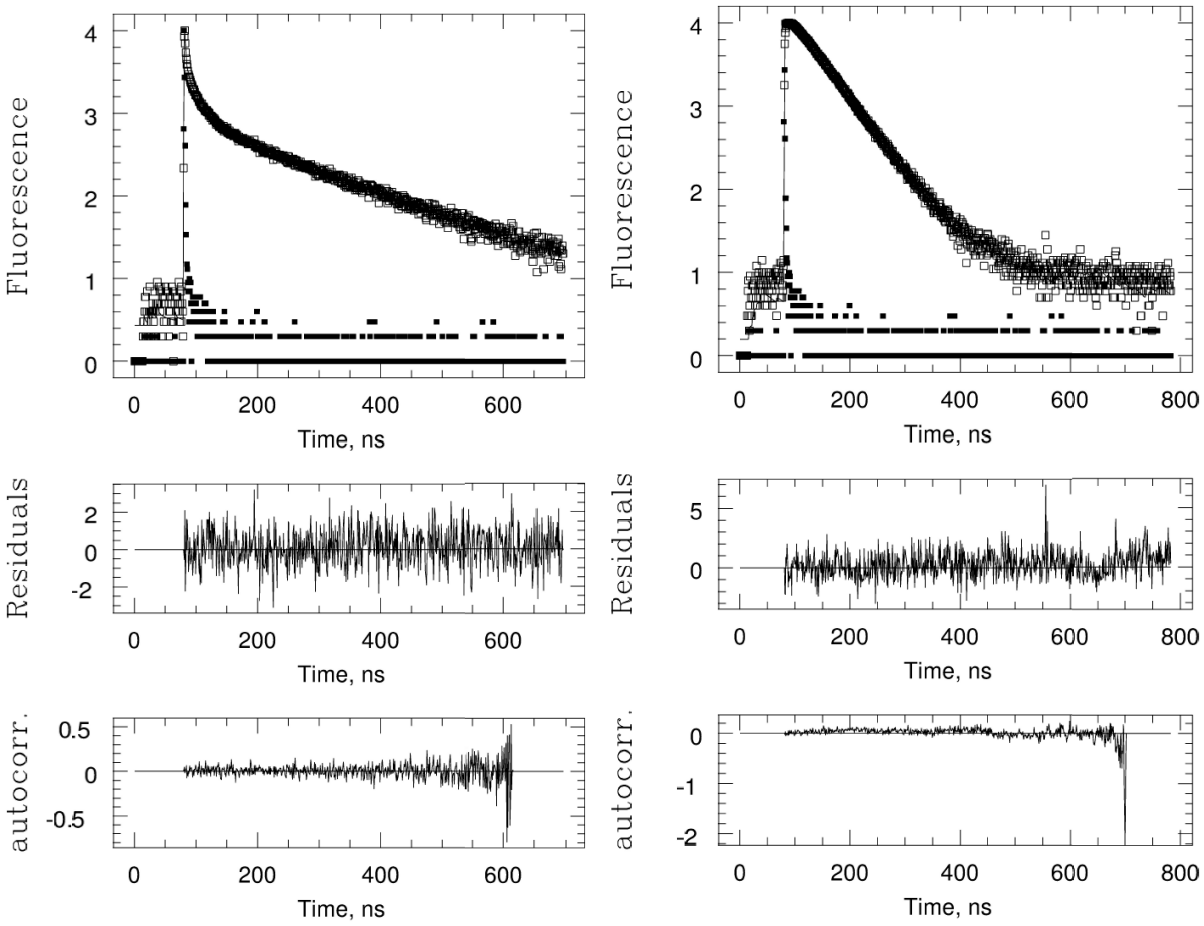


Figure S12. SPC of compound CyPy4 in DMF. On the right the monomer decay and on the left the excimer decay.

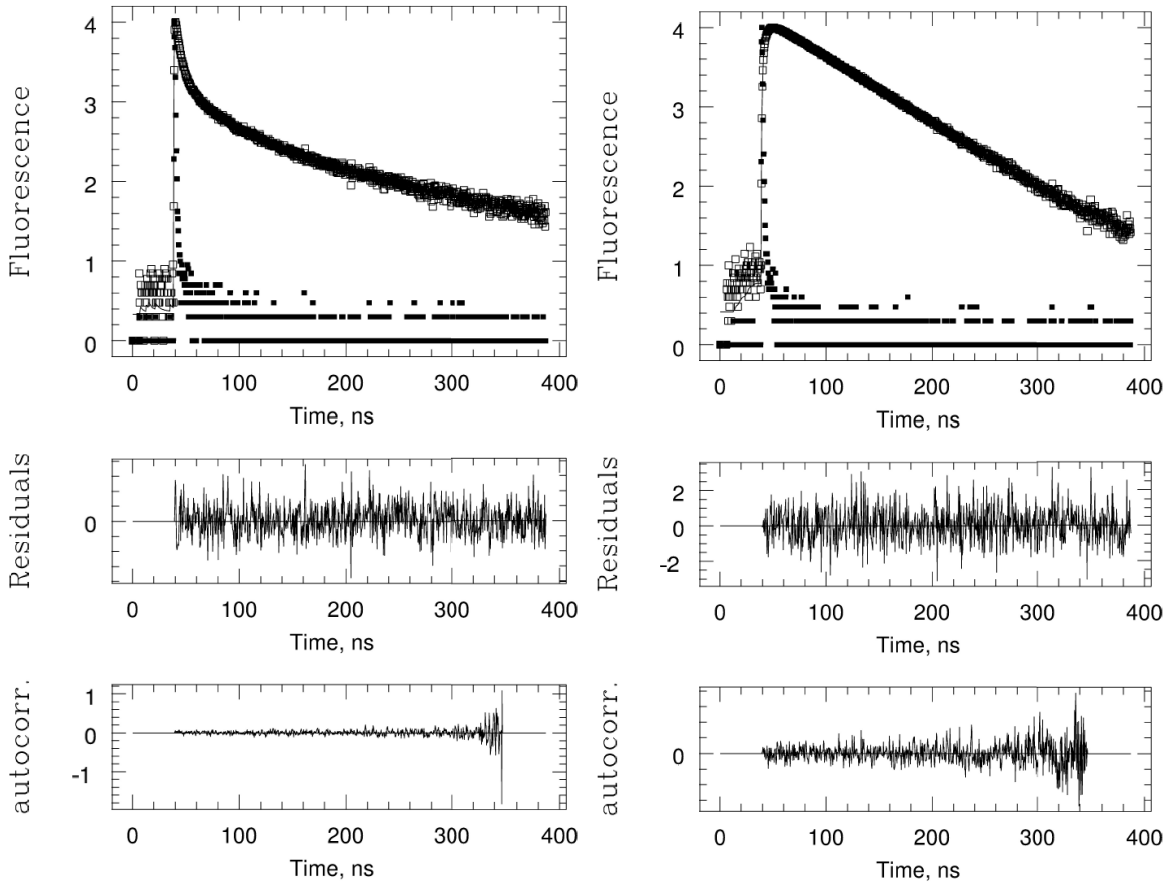


Figure S13. SPC of compound CyPy8 in DMF. On the right the monomer decay and on the left the excimer decay.

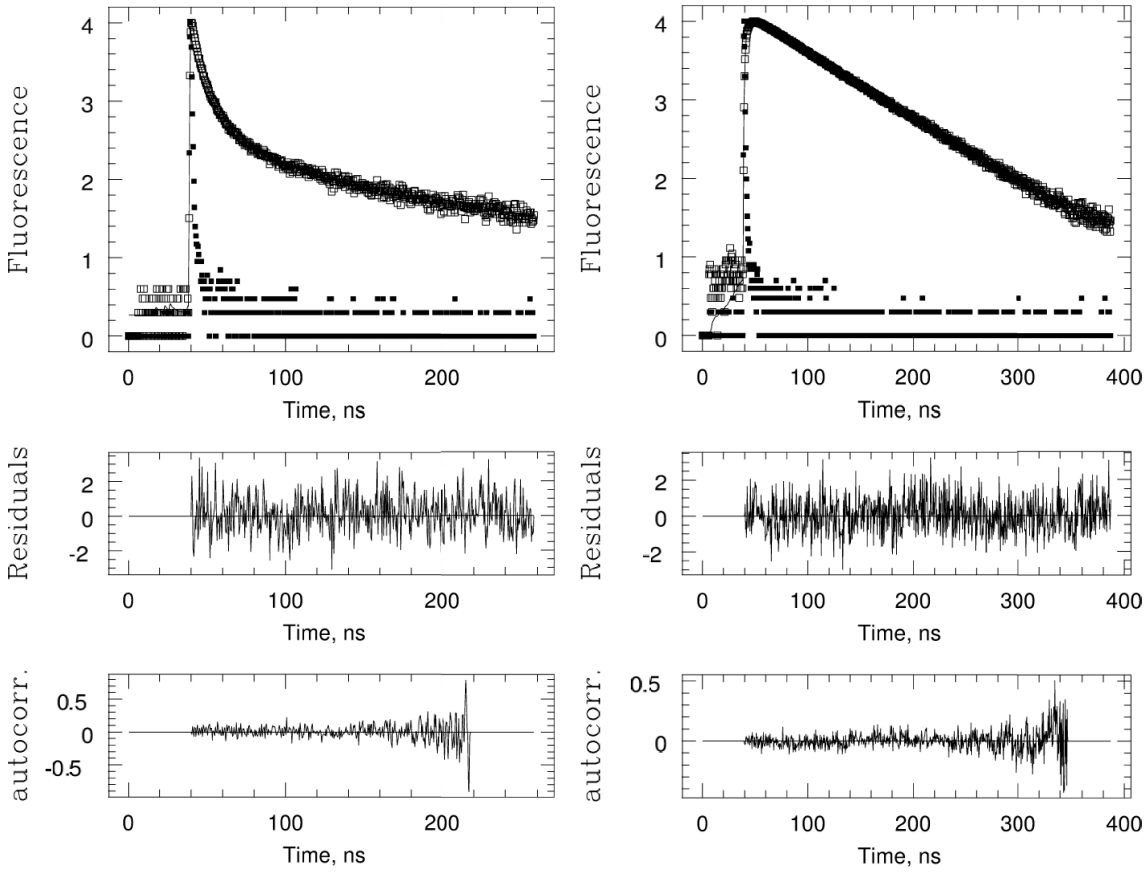


Figure S14. SPC of compound CyPy16 in DMF. On the right the monomer decay and on the left the excimer decay.

DMSO analysis

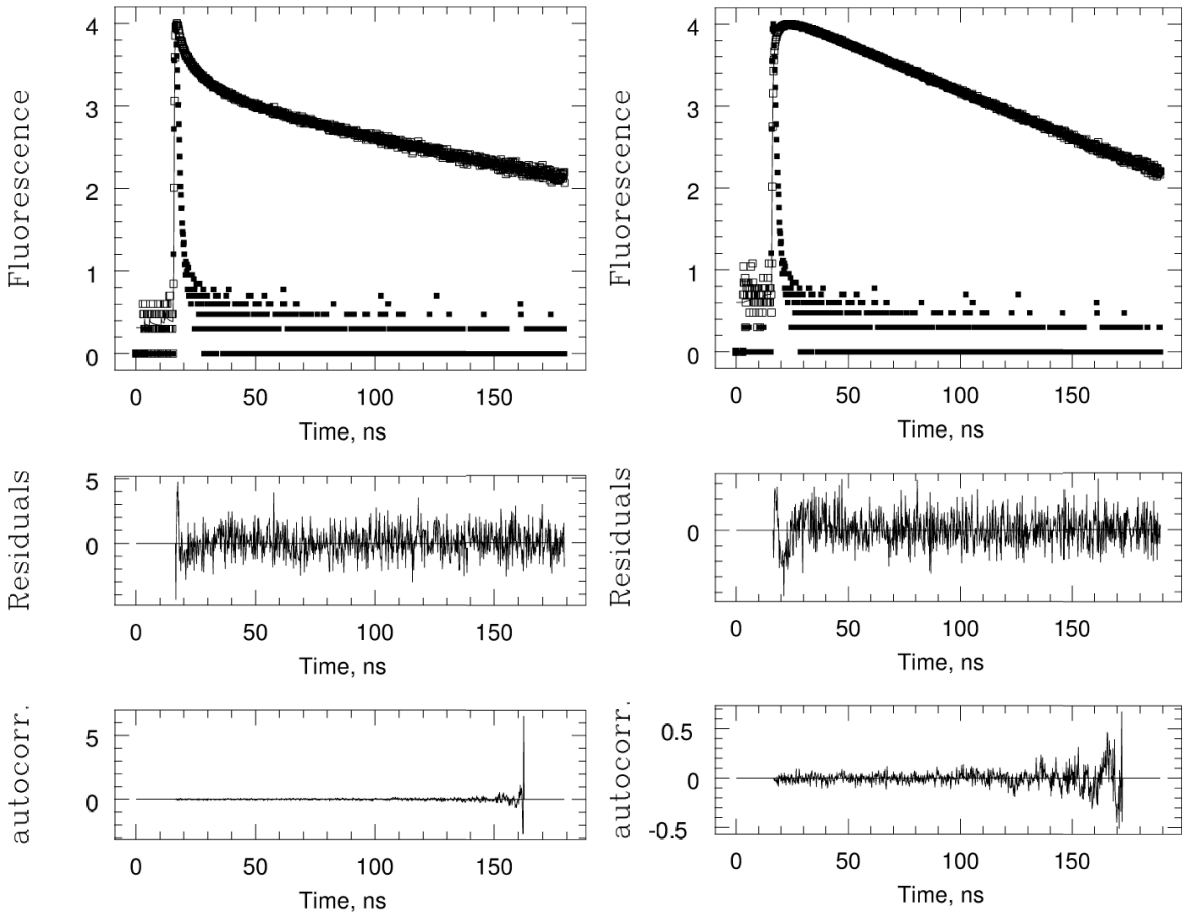


Figure S15. SPC of compound CyPy4 in DMSO. On the right the monomer decay and on the left the excimer decay.

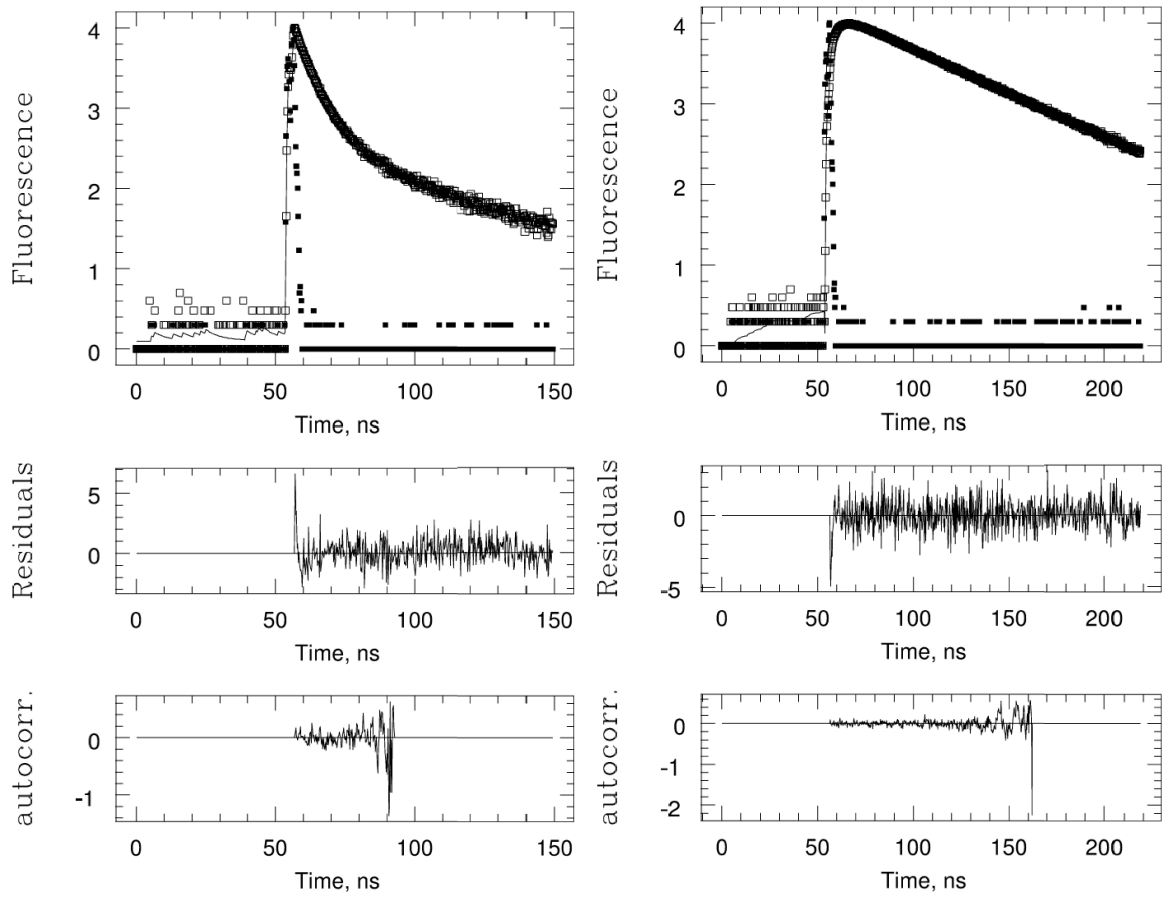


Figure S16. SPC of compound CyPy8 in DMSO. On the right the monomer decay and on the left the excimer decay.

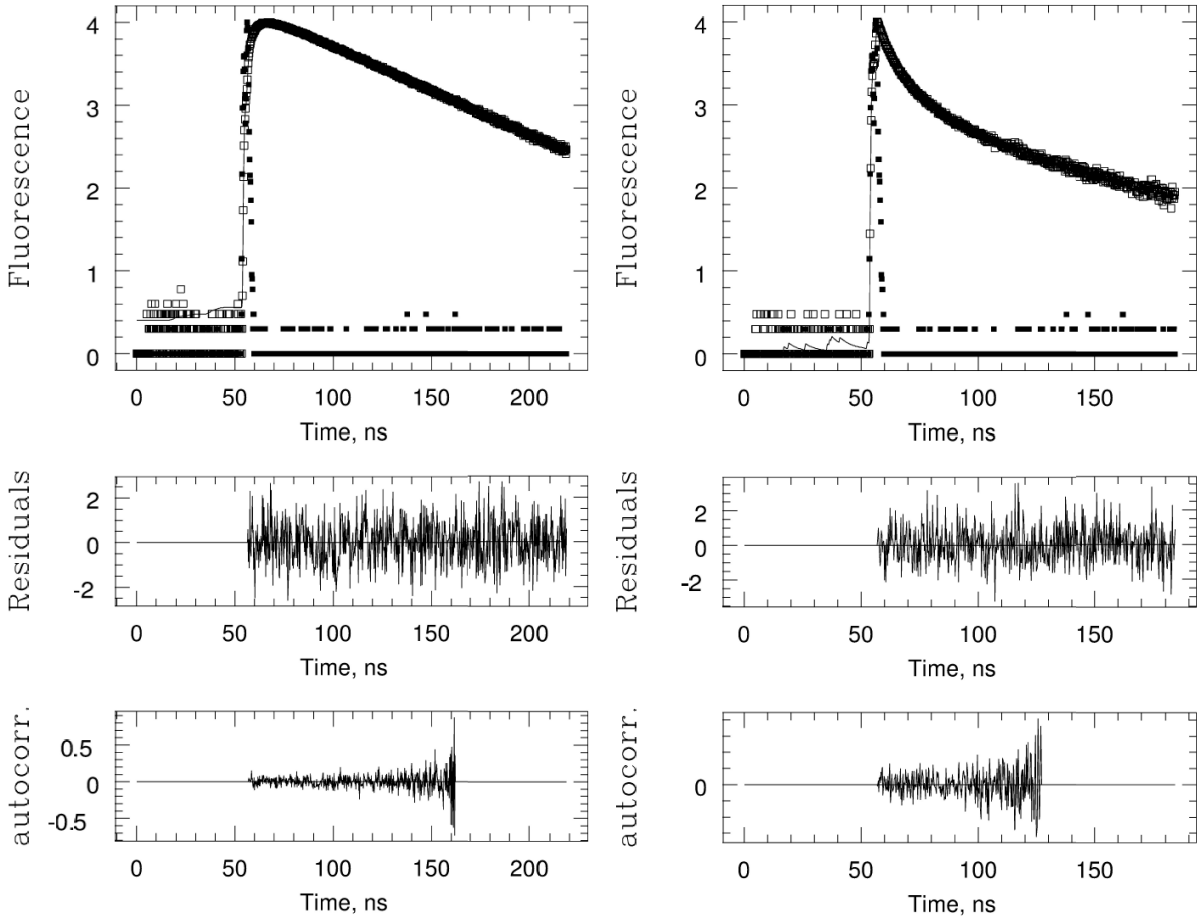


Figure S17. SPC of compound CyPy16 in DMSO. On the right the monomer decay and on the left the excimer decay.

Quenching studies

THF

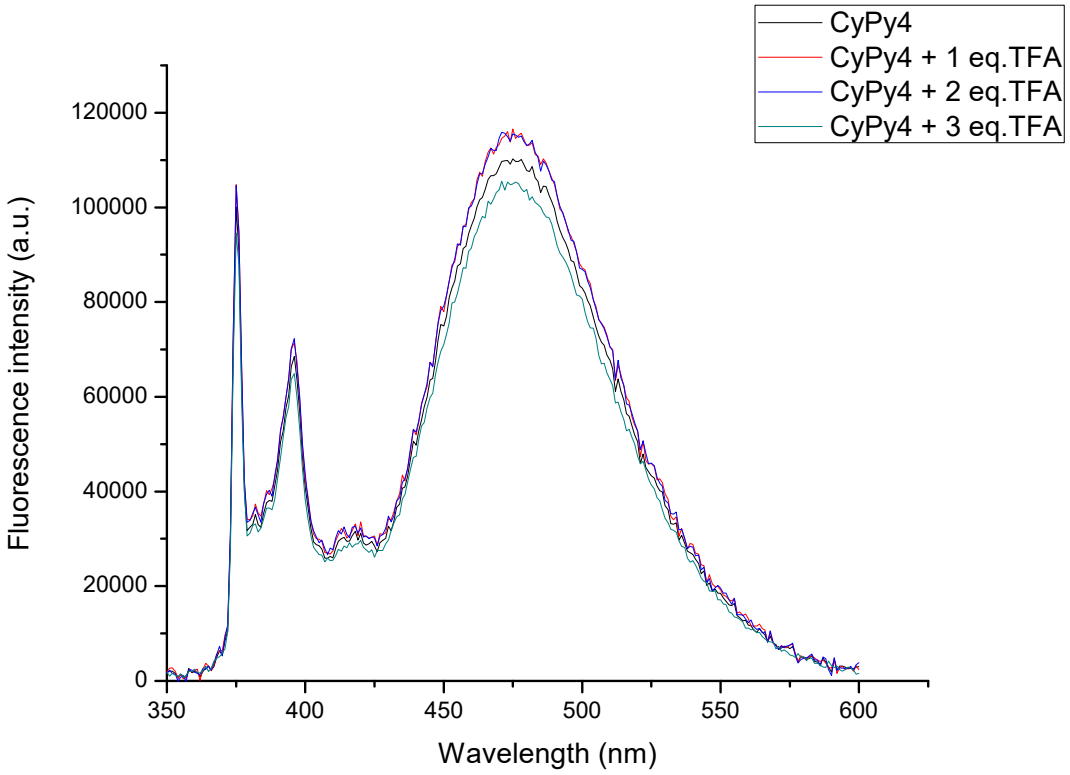


Figure S18. SSF of compound CyPy4 in THF

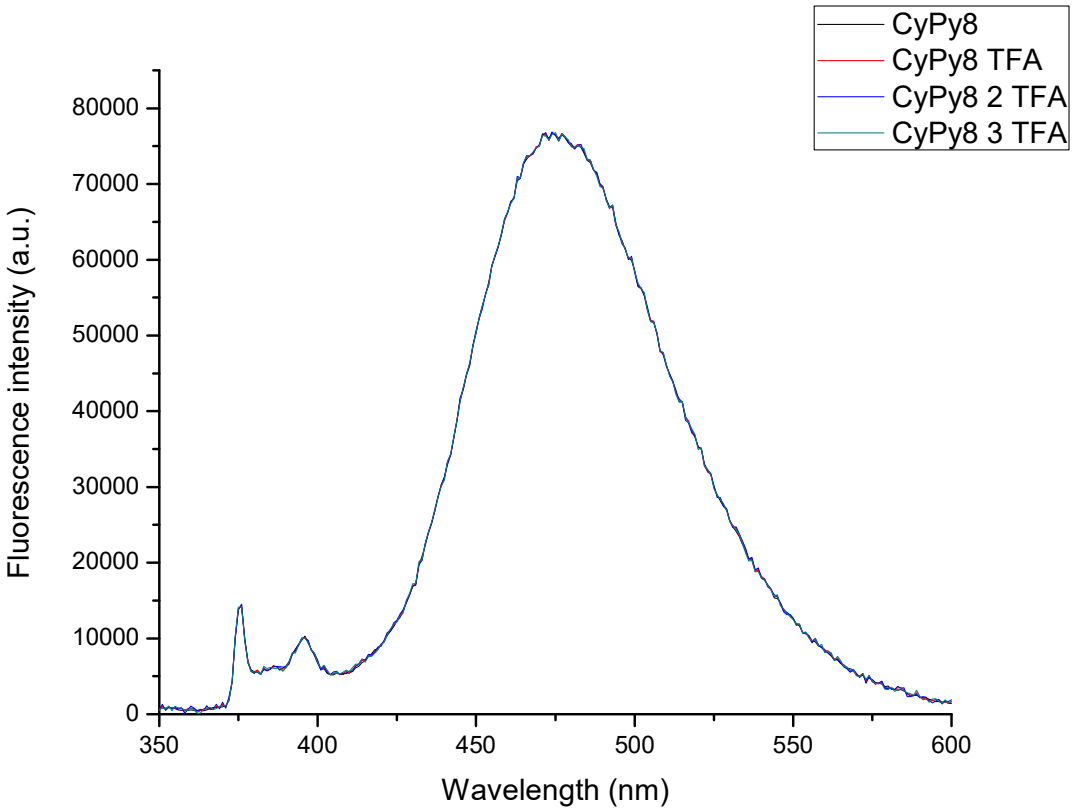


Figure S19. SSF of compound CyPy8 in THF

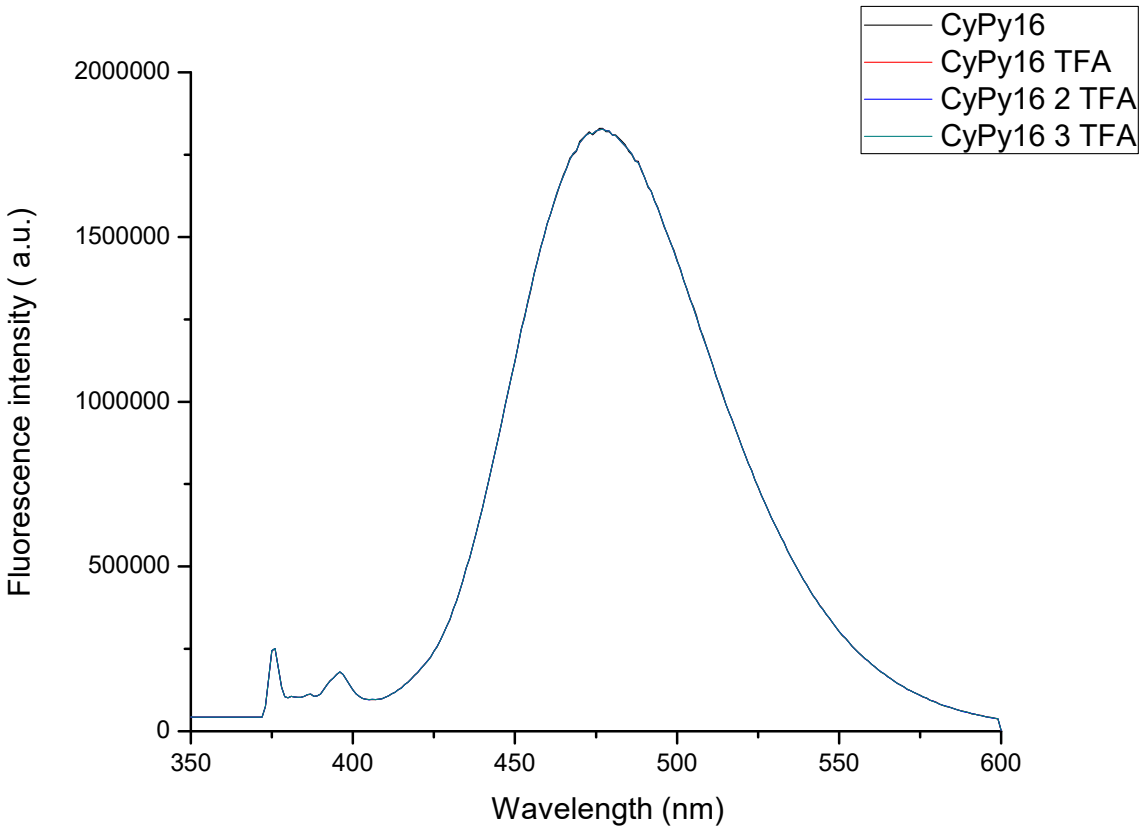


Figure S20. SSF of compound CyPy16 in THF

DMF

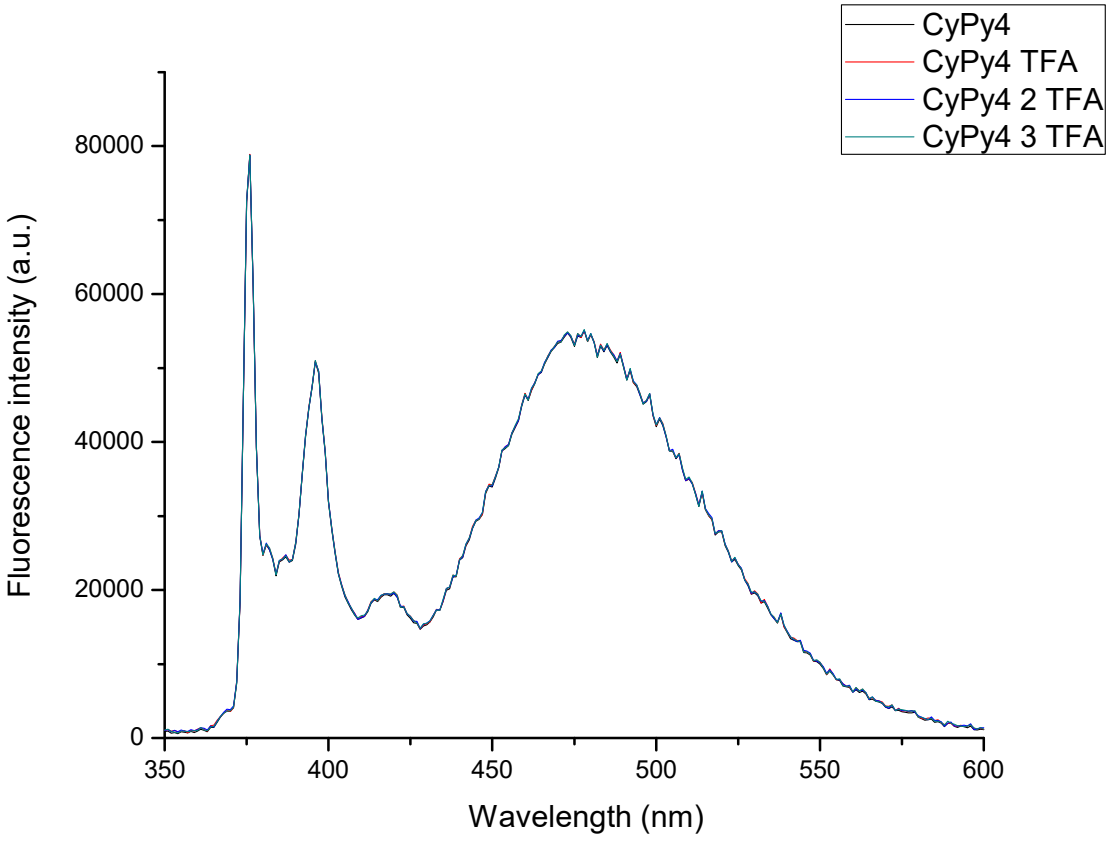


Figure S21. SSF of compound CyPy4 in DMF

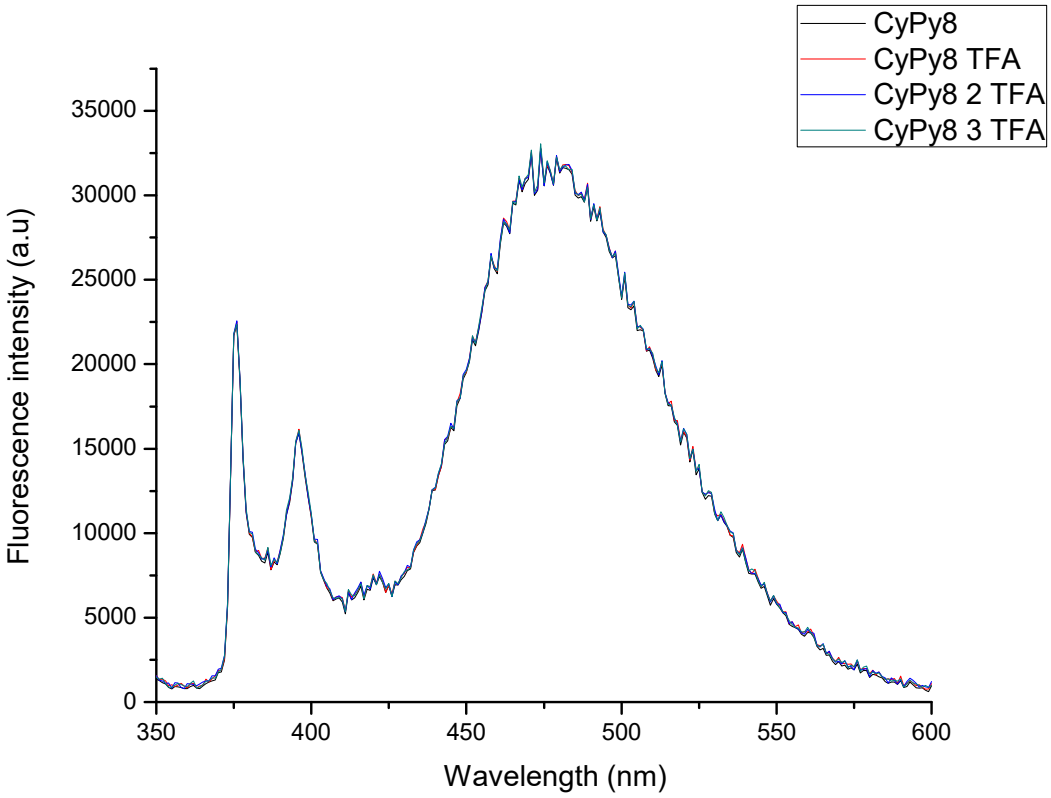


Figure S22. SSF of compound CyPy8 in DMF

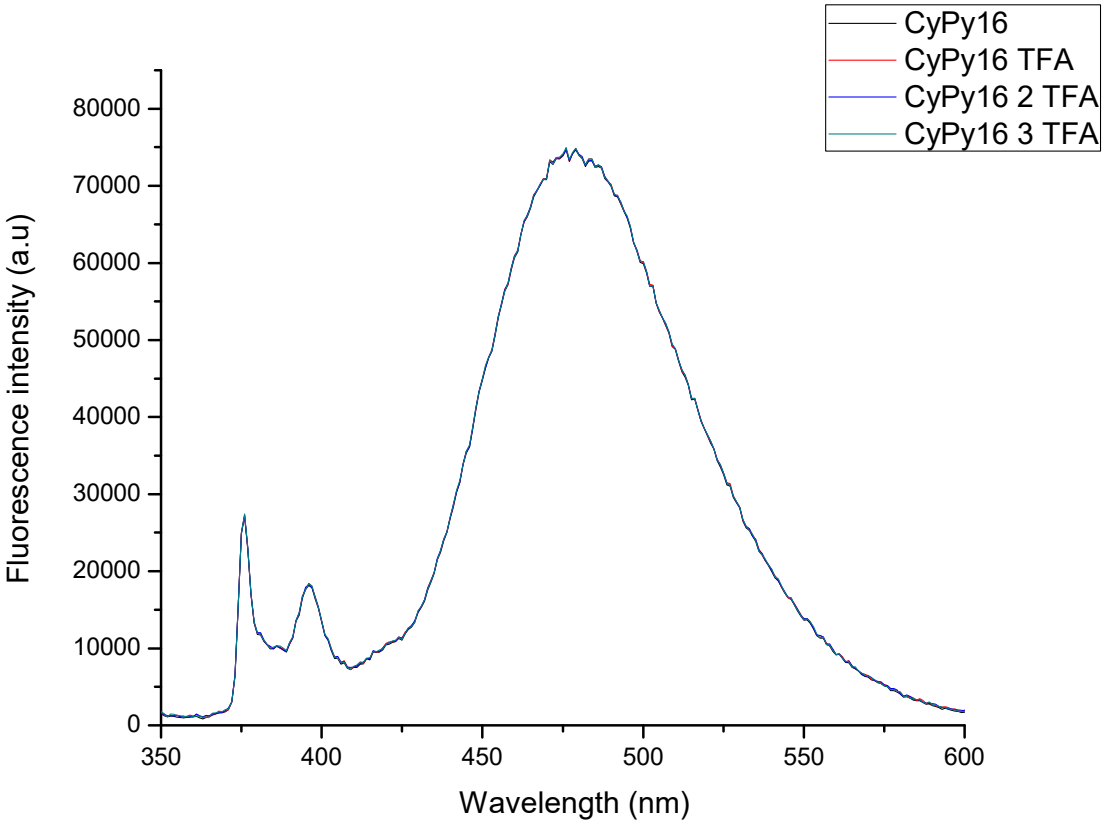


Figure S23. SSF of compound CyPy16 in DMF

DMSO

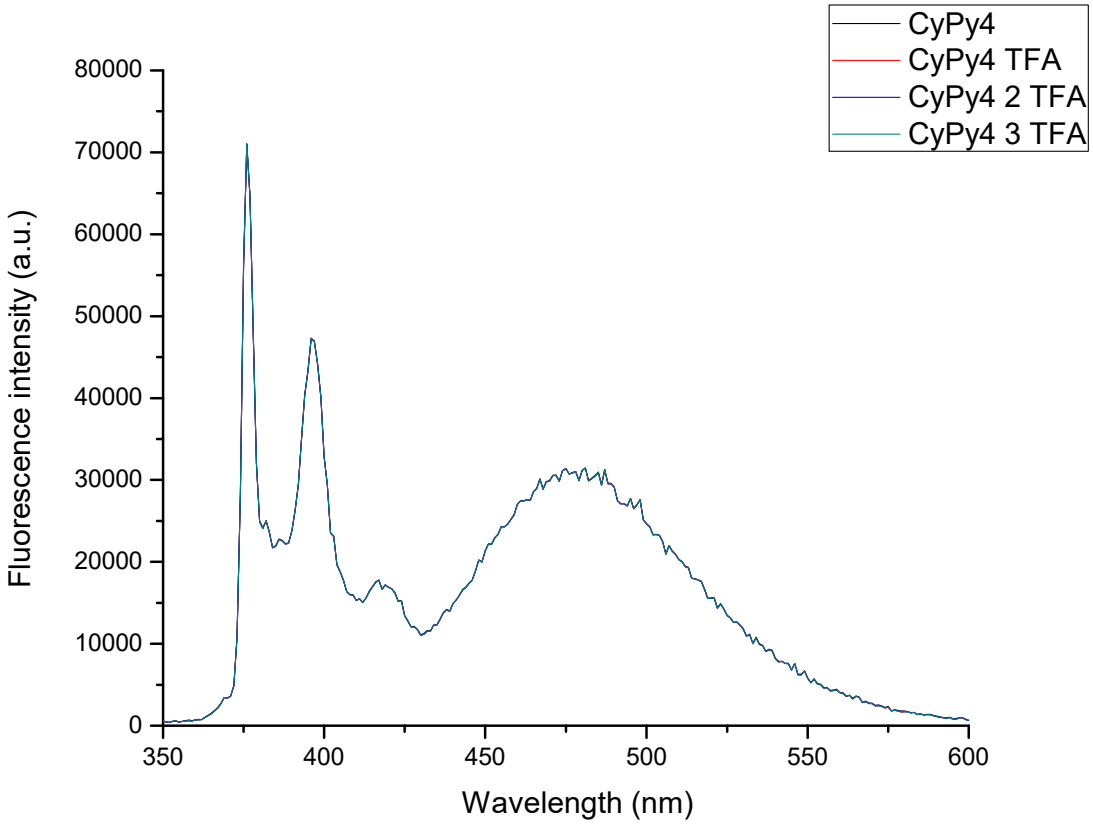


Figure S24. SSF of compound CyPy4 in DMSO

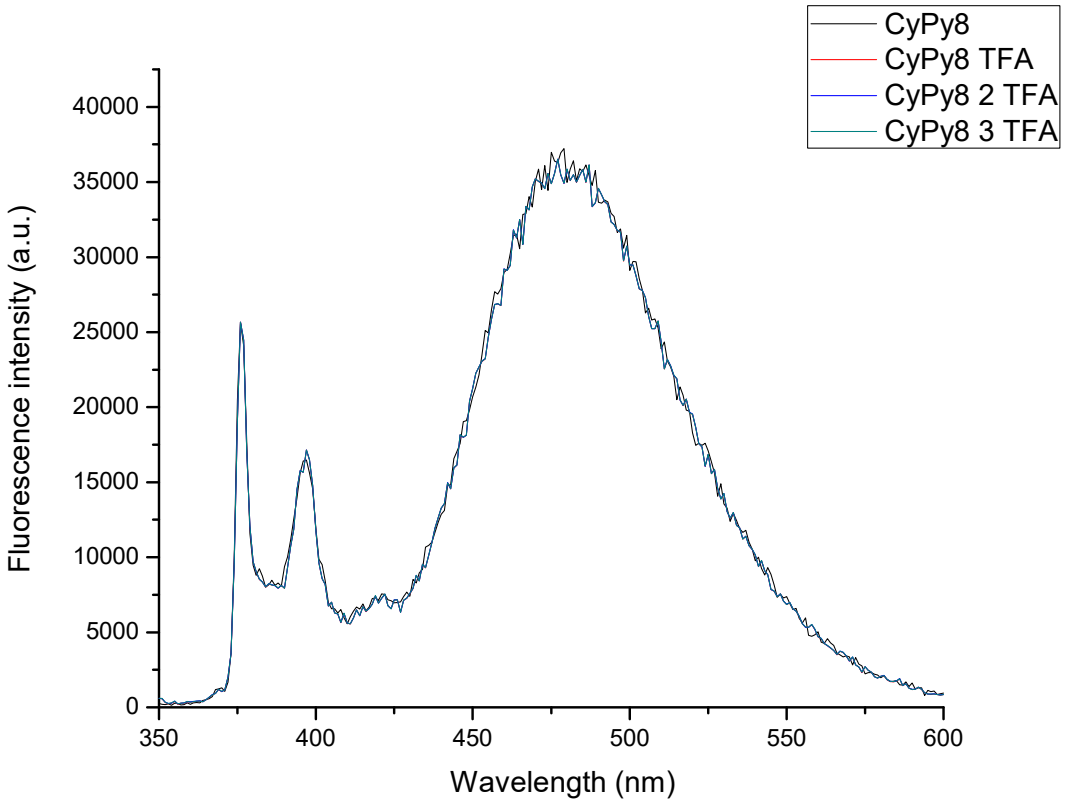


Figure S25. SSF of compound CyPy8 in DMSO

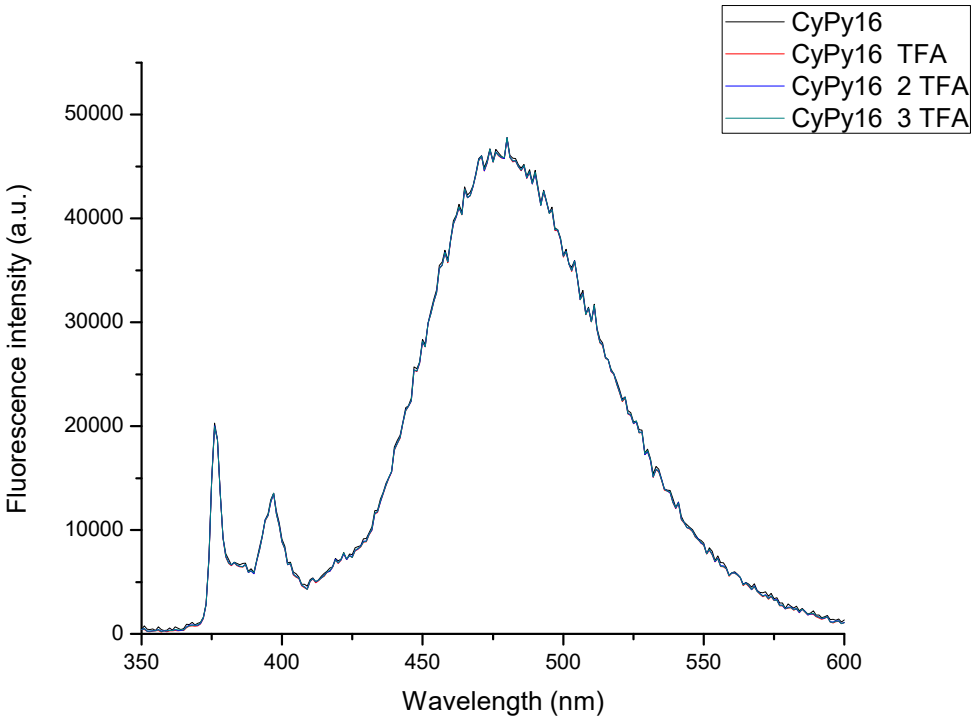


Figure S26. SSF of compound CyPy16 in DMSO

References

[1] G. Zaragoza-Galán, M.A. Fowler, J. Duhamel, R. Rein, N. Solladié, E. Rivera, Langmuir 28 (2012) 11195–11205.

[2] M. Vonlanthen, A. Cevallos-Vallejo, E. Aguilar-Ortíz, A. Ruiu, P. Porcu, E. Rivera, Polymer 99 (2016) 13–20.

[3] A. Cevallos-Vallejo, M. Vonlanthen, P. Porcu, A. Ruiu, E. Rivera, Tetrahedron Lett. 58 (2017) 1319–1323.