Chapter 3 Measurement of photoluminescence quantum yields using standard reference materials

Electronic supporting information

Contents

This Supporting information for Chapter 3 provides analytical data (HPLC), absorption, excitation, and emission spectra, and fluorescence lifetime measurements (Time Correlated Single Photon Counting) of the compounds used. Details of the measurements are given in Chapter 2. The LCMS measurements were carried out in MeCN:H_2O = 1:1 with a Shimadzu LCMS2010A spectrometer with atmospheric pressure using chemical ionization.

pTP

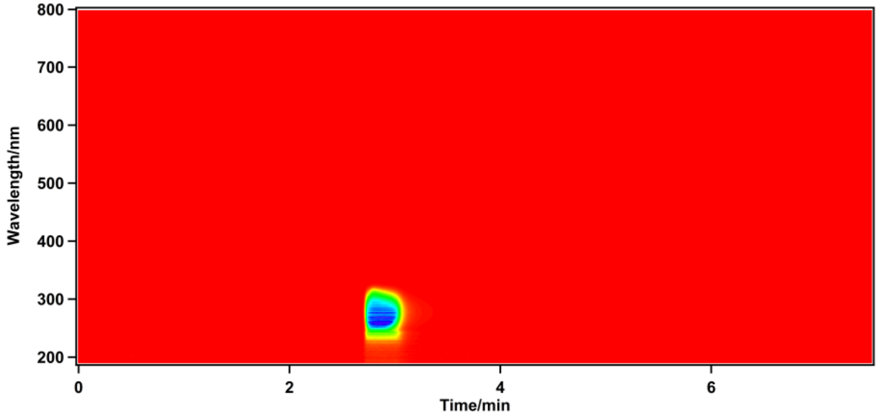

Figure S1. HPLC of p-terphenyl. Solvent and mobile phase: EtOAc/(heptane+ EtOAc) = 0.3

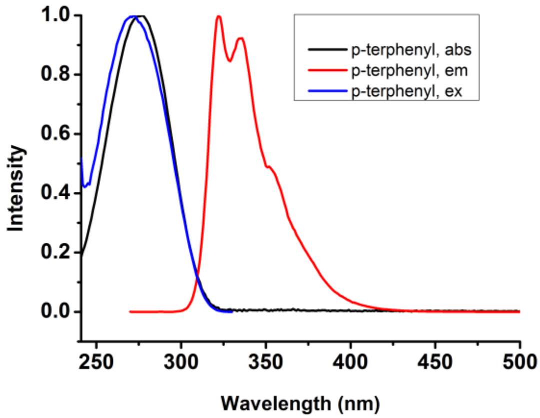

Figure S2. Normalized excitation (λ_{em} = 335 nm), emission (λ_{ex} = 263 nm), and absorption spectrum of p-terphenyl. Solvent: cyclohexane.

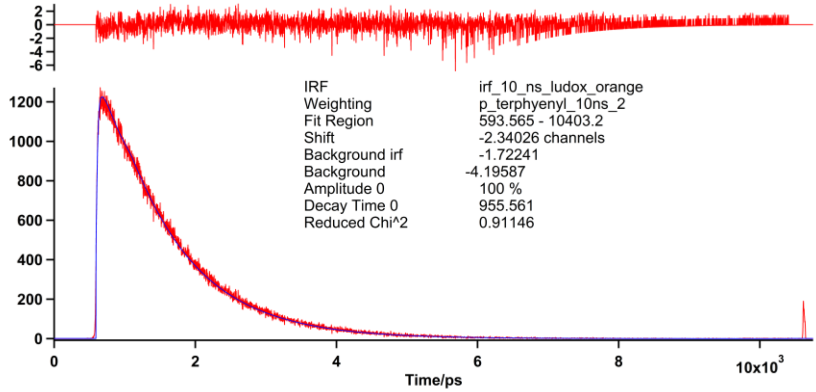

Figure S3. Fluorescence decay of p-terphenyl in cyclohexane (λ_{ex} = 304 nm, λ_{em} = 340 nm). The fitted lifetime (0.96 ns) is consistent with the literature (0.98 ± 0.03 ns)[1].

PPO

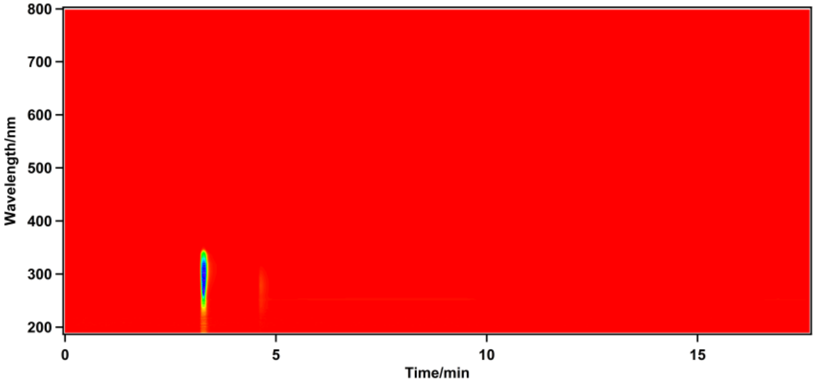

Figure S4. HPLC of PPO Solvent and mobile phase: EtOAc/(heptane + EtOAc) = 0.3. There are very few impurities at 4.5 min compared to the main peak at ~3 min, and they have similar absorption spectra.

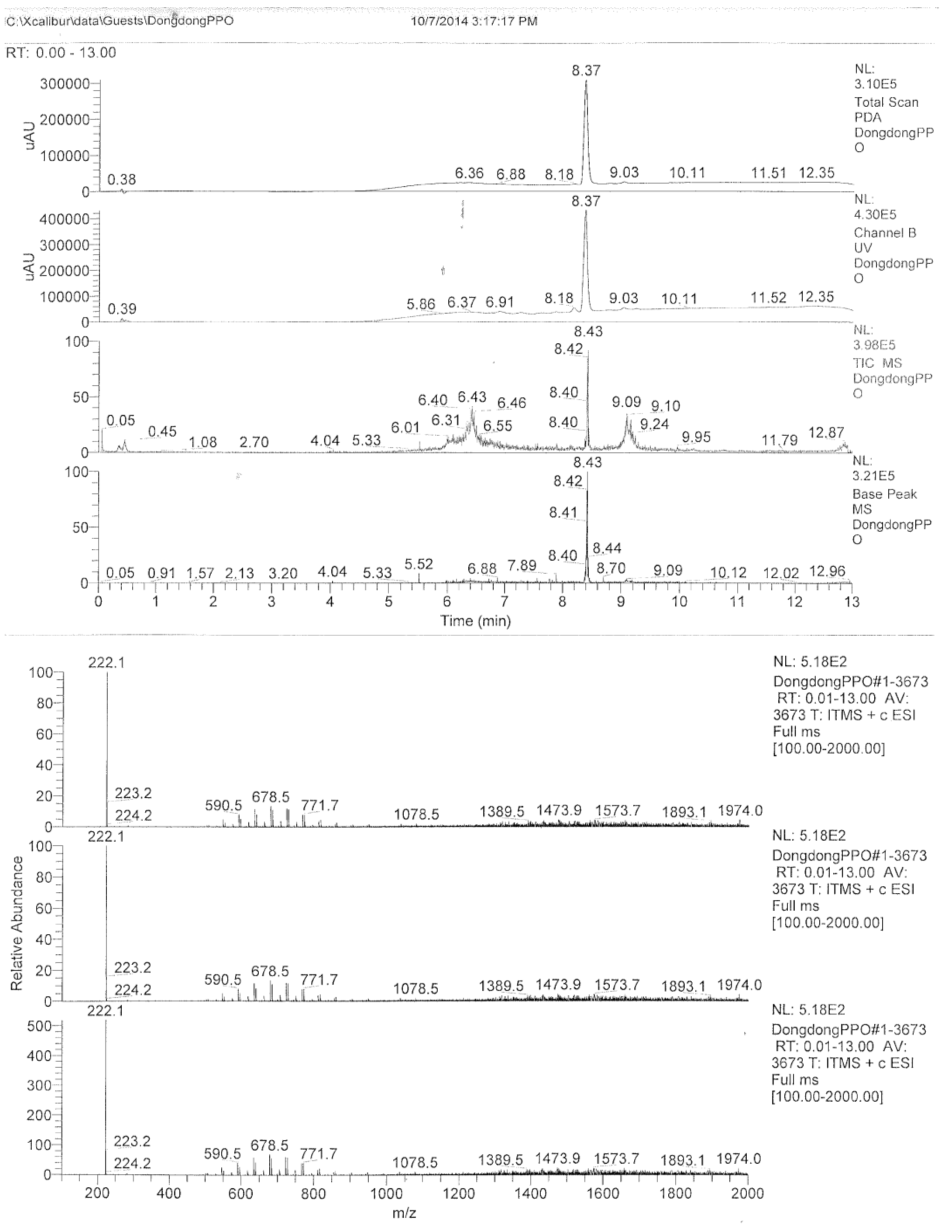

Figure S5. LCMS of PPO Solvent and mobile phase MeCN:H_2O=1:1.

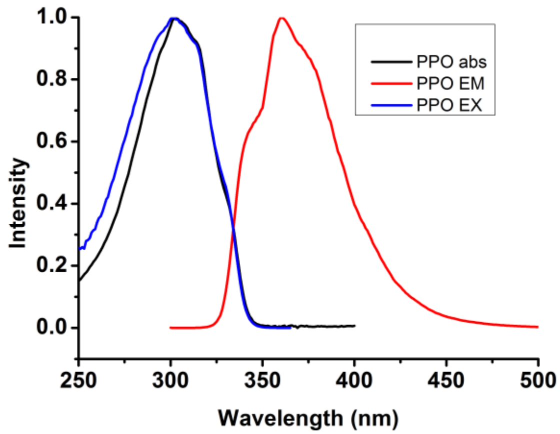

Figure S6. Normalized excitation (λ_{em} = 375 nm), emission (λ_{ex} = 295 nm), and absorption spectrum of PPO Solvent: MeOH.

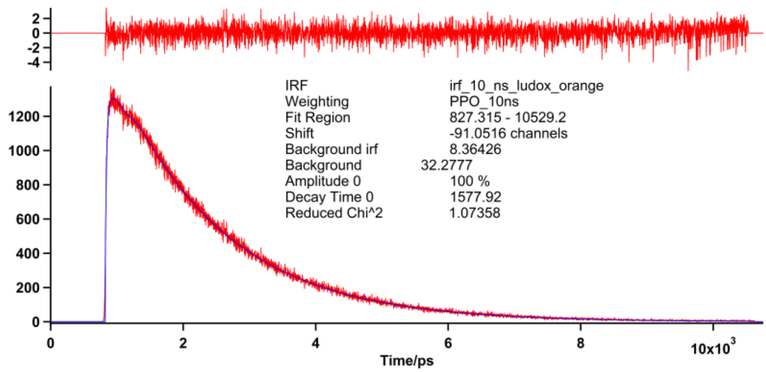

Figure S7 Fluorescence decay of PPO in MeOH (λ_{ex} = 304 nm, λ_{em} = 340 nm). The fitted lifetime (1.58 ns) is consistent with the literature (1.65 ± 0.05 ns).[1]

QD

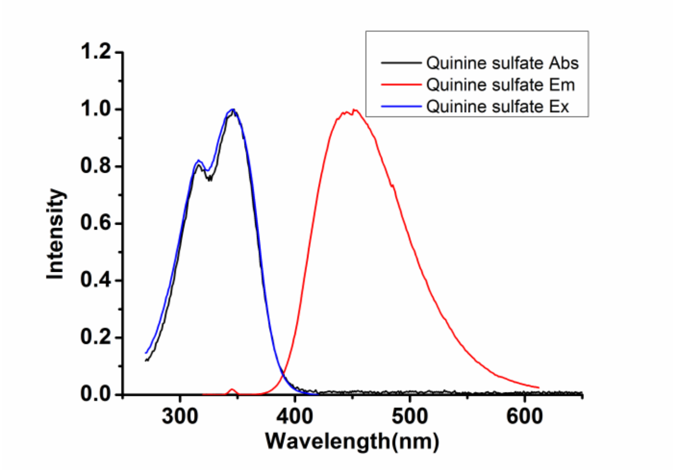

Figure S8. Normalized excitation (λ_{em} = 430 nm), emission (λ_{ex} = 320 nm), and absorption spectrum of QD. Solvent: 0.1 M $HClO_4$.

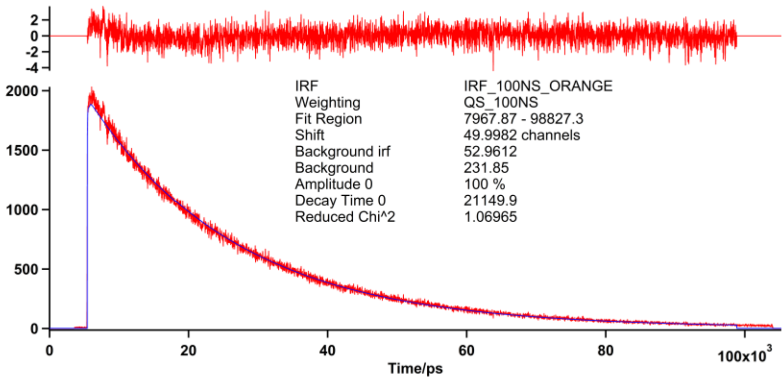

Figure S9 Fluorescence decay of Quinine Disulfate in 0.105 M $HClO_4$ (λ_{ex} = 304 nm, λ_{em}=455 nm). The fitted lifetime (21.15 ns) is slightly longer than the literature value (18.9 ± 0.3 ns),[2] which is measured in H_2SO_4. This is consistent with the higher QY in $HClO_4$ solution.

DPA

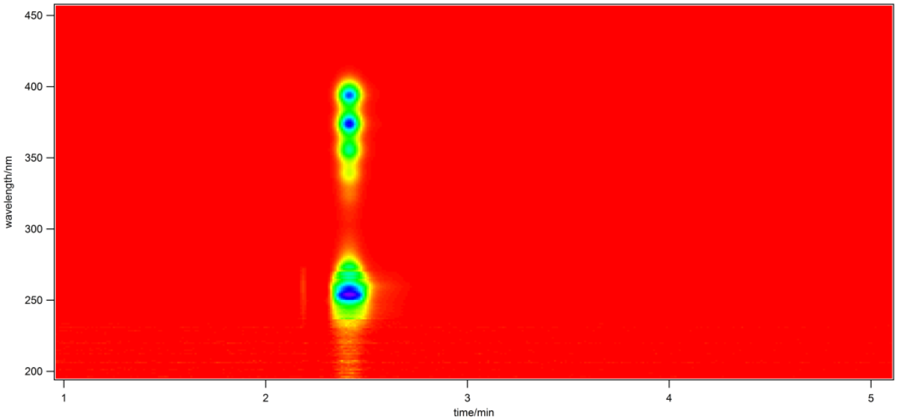

Figure S10. HPLC of DPA. Solvent and mobile phase: EtOAc/(heptane+ EtOAc) = 0.15.

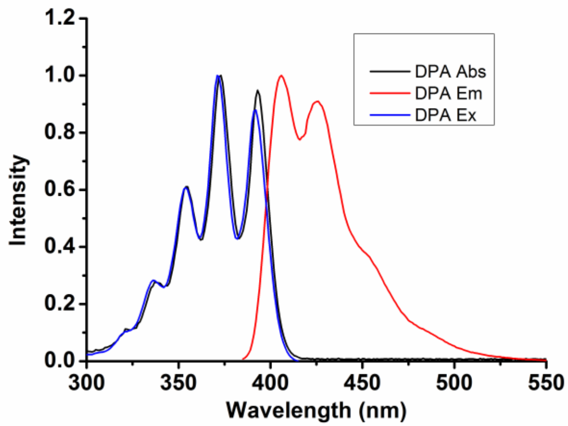

Figure S11. Normalized excitation (λ_{em} = 425 nm), emission (λ_{ex} = 375 nm), and absorption spectrum of DPA. Solvent: cyclohexane.

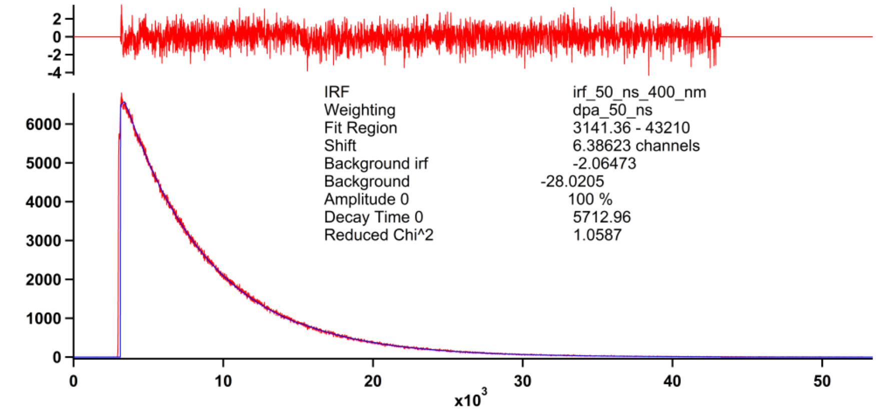

Figure S12 Fluorescence decay of DPA in cyclohexane (λ_{ex} = 400 nm, λ_{em} = 420 nm). The fitted lifetime (5.71 ns) is shorter than the literature value (7.5 $\pm$ 0.4 ns),[1] in which case the solvent is degassed.

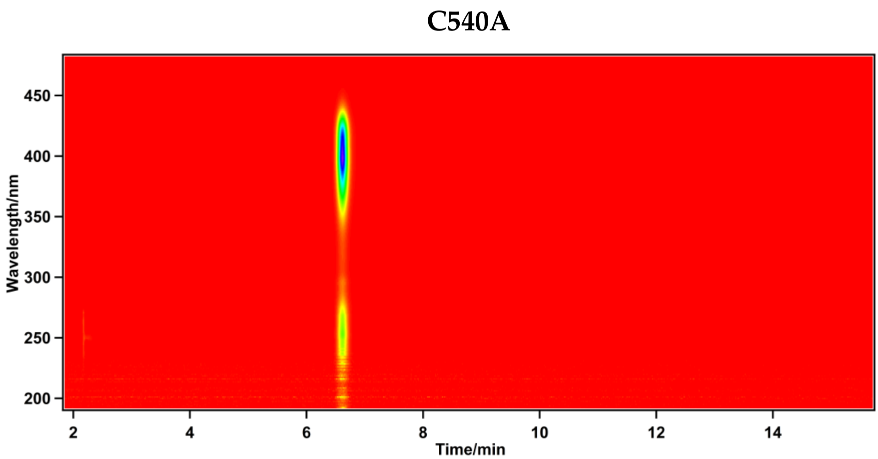

Figure S13. HPLC of C540A. Solvent and mobile phase: EtOAc/(heptane+ EtOAc) = 0.15.

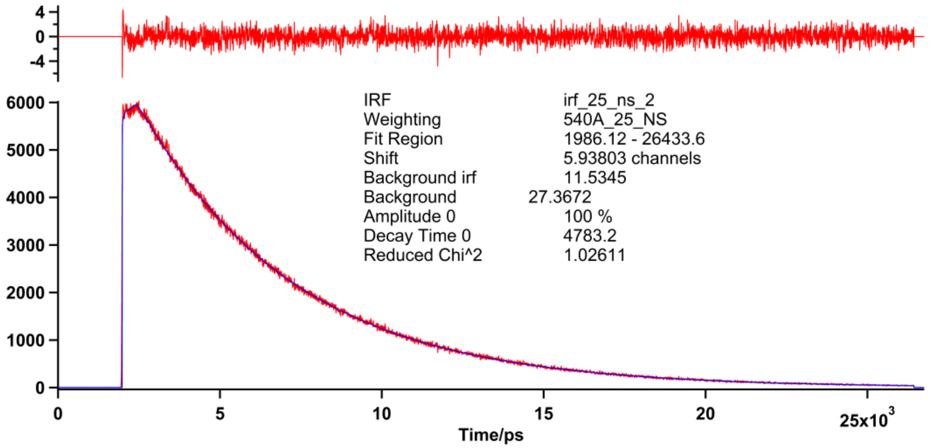

Figure S14 Fluorescence decay of C540A in EtOH (λ_{ex} = 400 nm, λ_{em}=520 nm). The fitted lifetime (4.78 ns) is in reasonable agreement with the literature (4.3 ± 0.2 ns).[1]

Ru(bpy)3

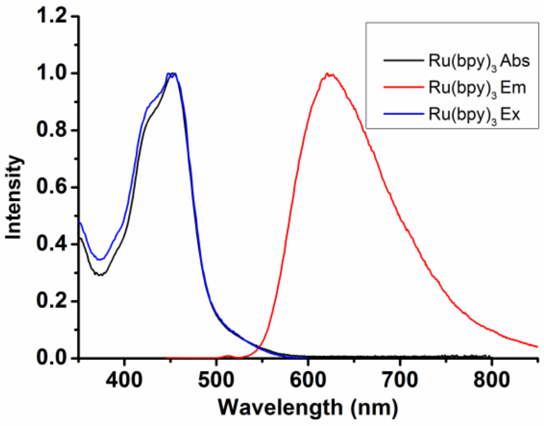

Figure S15 Normalized excitation (λ_{em} = 610 nm), emission (λ_{ex} = 440 nm), and absorption spectrum of $Ru(bpy)_3$. Solvent: H_2O.

Coumarin 540

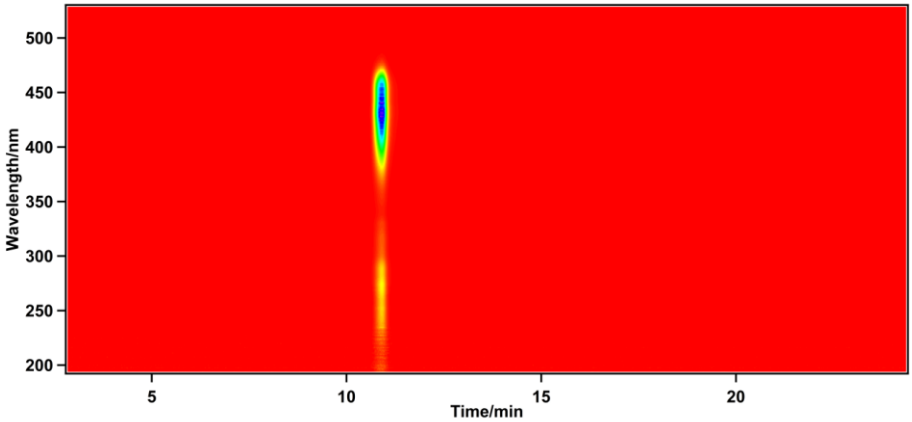

Figure S16 HPLC of C540. Solvent and mobile phase: EtOAc/(heptane+ EtOAc) = 0.15

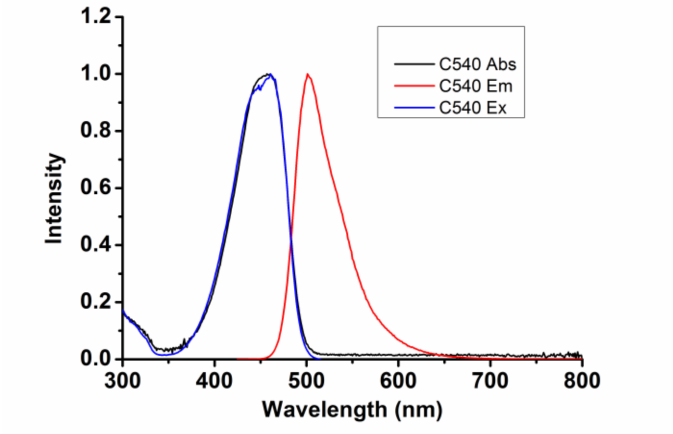

Figure S17 Normalized excitation (λ_{em} = 510 nm), emission (λ_{ex} = 420 nm), and absorption spectrum of coumarin 540. Solvent: EtOH.

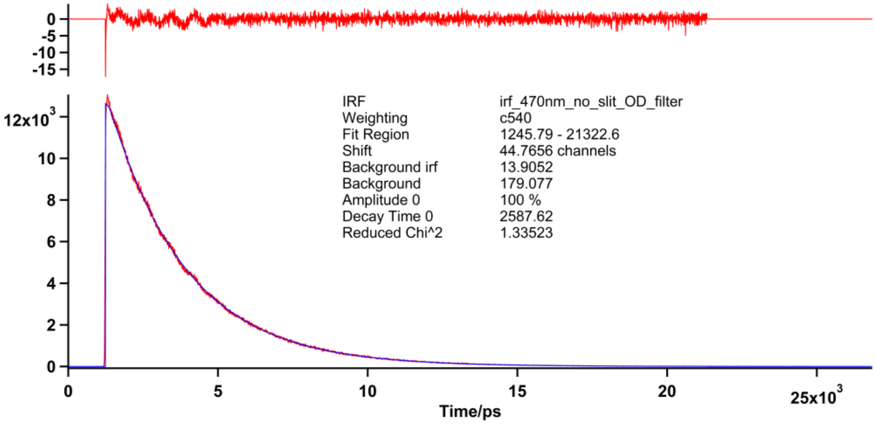

Figure S18 Fluorescence decay of C540 in EtOH (λ_{ex} = 450 nm, λ_{em} = 505 nm). The fitted lifetime (2.59 ns) is in agreement with the literature (2.56 ns).[5]

Coumarin 480

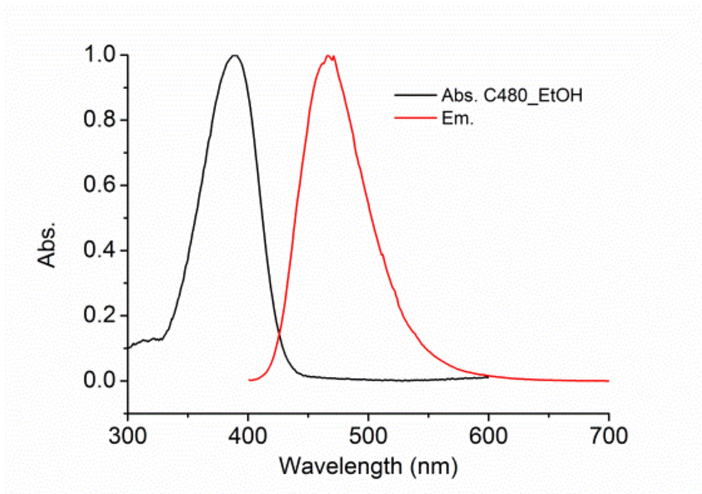

Figure S19 Normalized absorption and emission (λ_{ex} = 390 nm) spectra of C480 in EtOH.

Fluoresceine

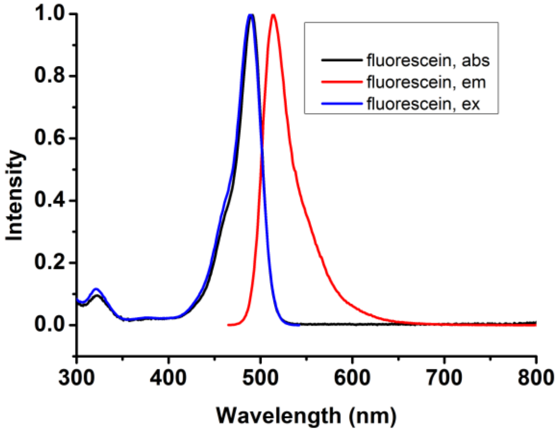

Figure S20 Normalized excitation (λ_{em} = 550 nm), emission (λ_{ex} = 450 nm), and absorption spectrum of fluorescein. Solvent: 0.1 M NaOH.

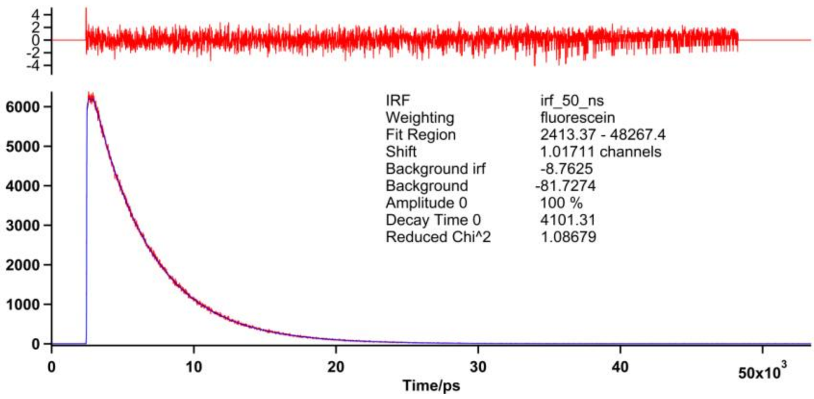

Figure S21 Fluorescence decay of fluoresceine in 0.1 M NaOH (λ_{ex} = 488 nm, λ_{em} = 507 nm). The fitted lifetime (4.10 ns) is consistent with the literature (4.00 ns).[3]

Rhodamine 6G

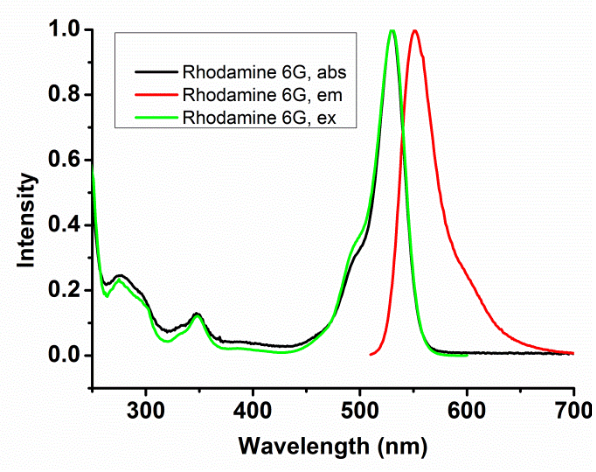

Figure S22 Normalized excitation (λ_{em} = 610 nm), emission (λ_{ex} = 500 nm), and absorption spectrum of R6G. Solvent: EtOH.

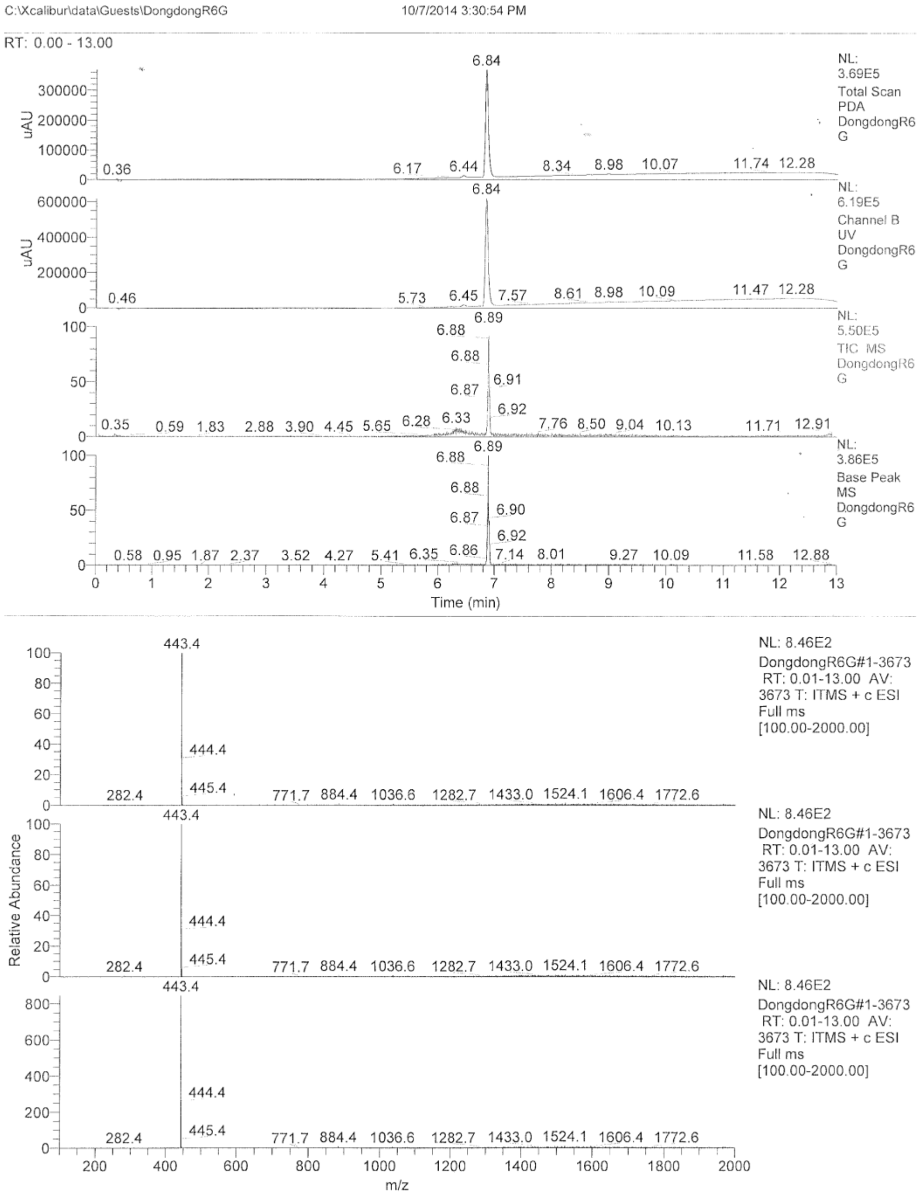

Figure S23 LCMS of R6G. Solvent and mobile phase MeCN:H_2O=1:1.

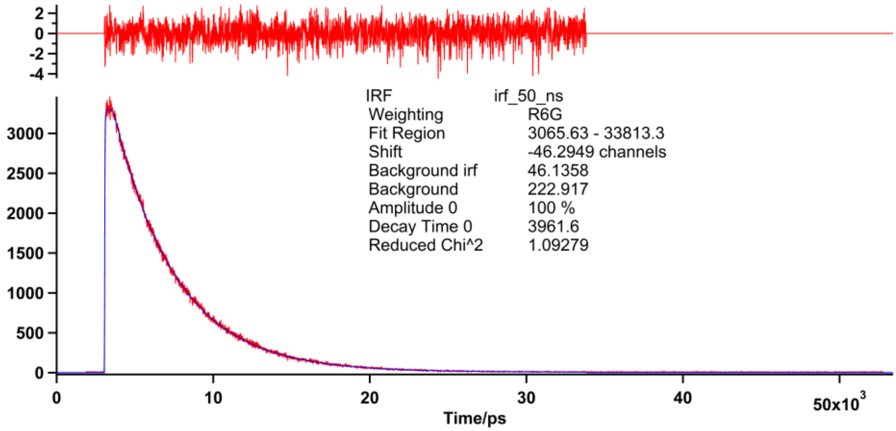

Figure S24 Fluorescence decay of Rhodamine 6G in EtOH (λ_{ex} = 488 nm, λ_{em}=550 nm). The fitted lifetime (3.96 ns) is in agreement with the literature (3.99 ns).[4]

DCM

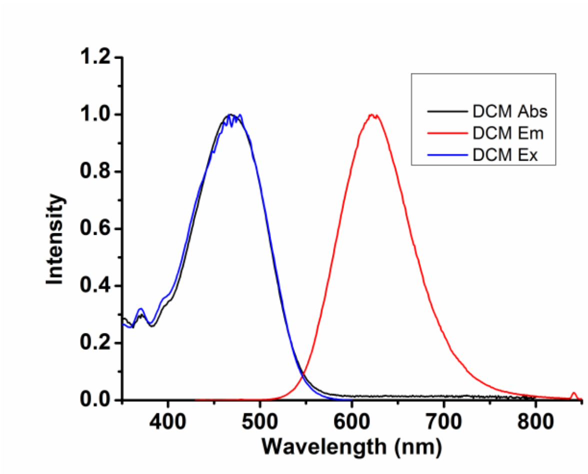

Figure S25 Normalized excitation (λ_{em} = 610 nm), emission (λ_{ex} = 500 nm), and absorption spectrum of DCM. Solvent: EtOH.

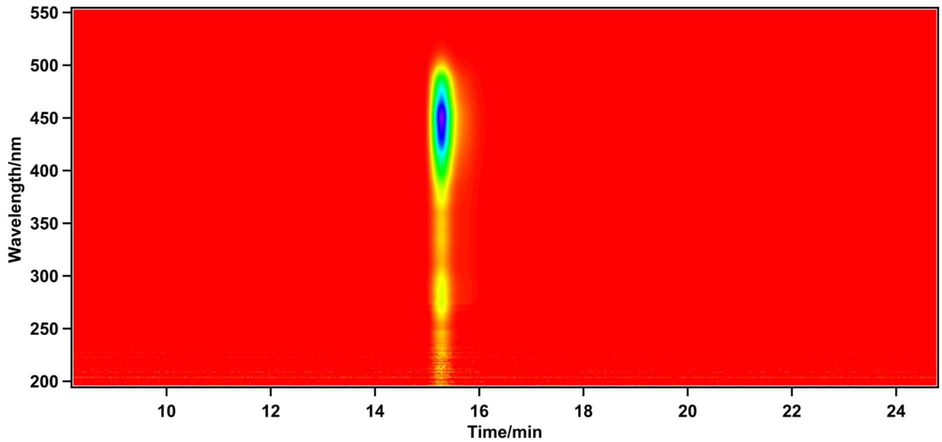

Figure S26 HPLC of DCM. Solvent and mobile phase: EtOAc/(heptane+ EtOAc) = 0.15

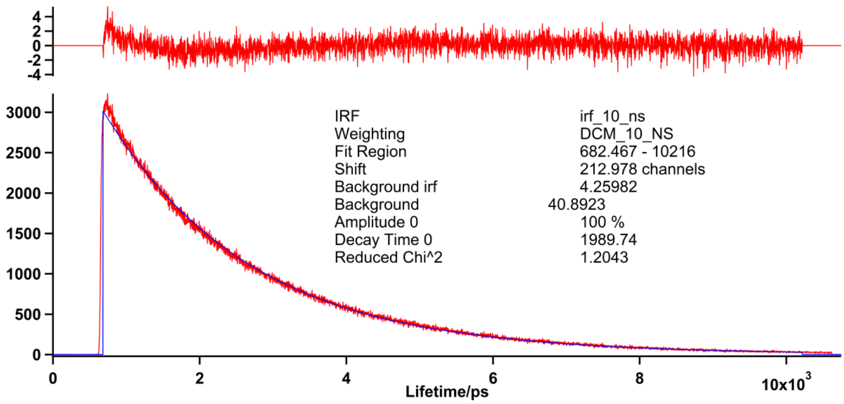

Figure S27 Fluorescence decay of DCM in EtOH (λ_{ex} = 450 nm, λ_{em} = 650 nm). The fitted lifetime (1.99 ns) is in reasonable agreement with the literature (1.8 ns),[6] but the fit is not very good.

PeryOr

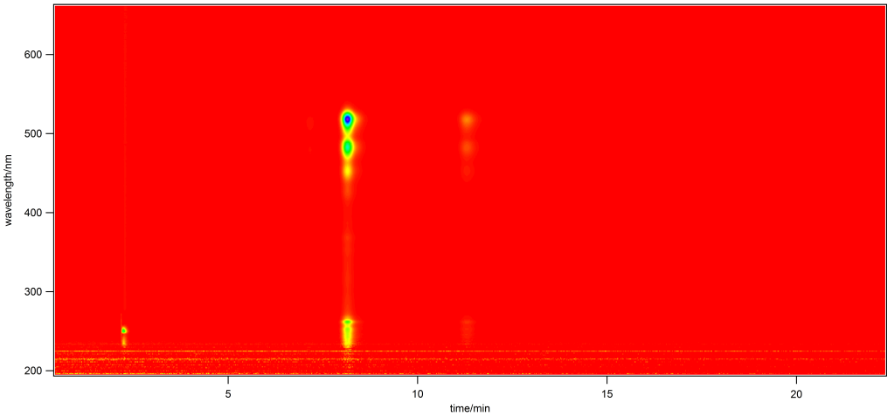

Figure S28 HPLC of perylene orange. Solvent and mobile phase: EtOAc/(heptane+ EtOAc) = 0.15. There is a minor impurity at ~12 min, which has the same absorption spectrum as that of ~8.5 min main peak.

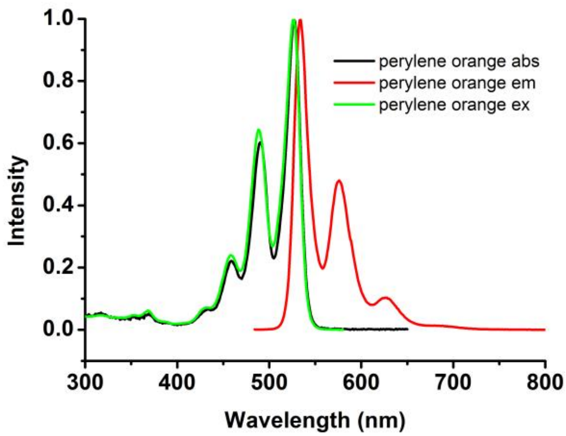

Figure S29 Normalized excitation (λ_{em} = 600 nm), emission (λ_{ex} = 470 nm), and absorption spectrum of perylene orange. Solvent: chloroform.

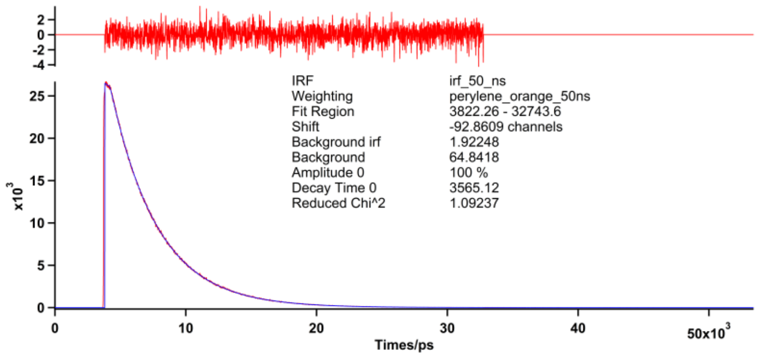

Figure S30 Fluorescence decay of perylene orange in chloroform (λ_{ex} = 488 nm, λ_{em} = 535 nm). The fitted lifetime (3.57 ns) is agreement with the literature (3.6 ns).[5]

Erythrosin B

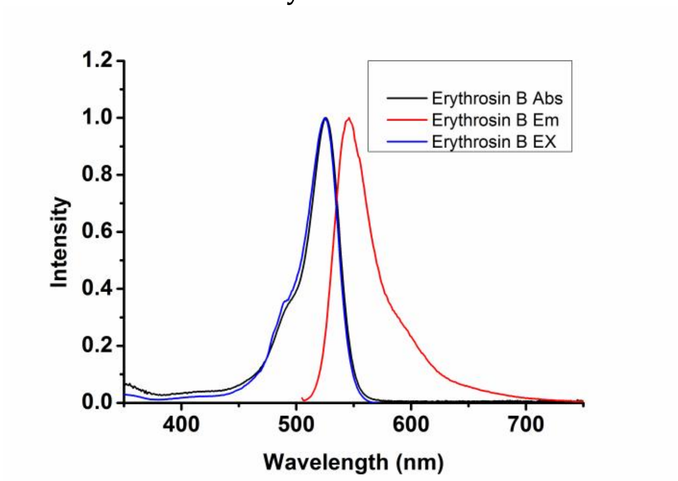

Figure S31 Normalized excitation (λ_{em} = 580 nm), emission (λ_{ex} = 500 nm), and absorption spectrum of Erythrosin B. Solvent: MeOH.

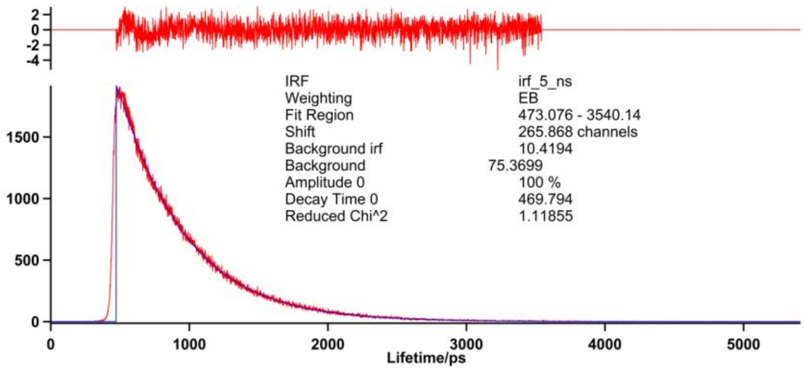

Figure S32 Fluorescence decay of EB in MeOH (λ_{ex} = 490 nm, λ_{em} = 560 nm). The fitted lifetime (0.47 ns) is in agreement with the literature (0.47 ns).[6]

ZnTPP

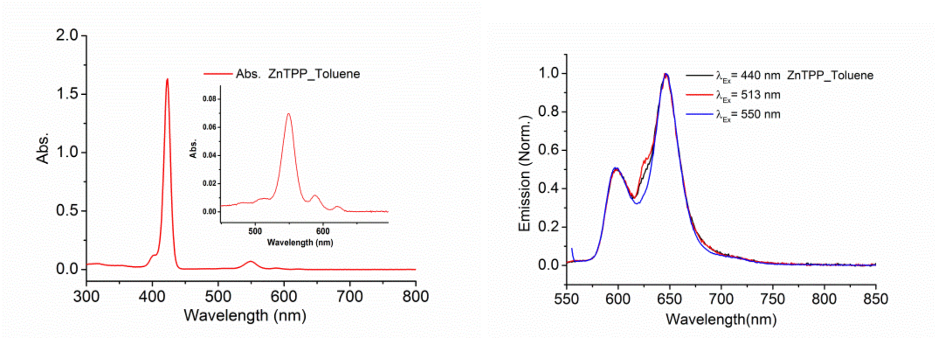

Figure S33 Absorption and emission (normalized, λ_{ex} = 440, 513 and 550 nm) spectra of ZnTPP. Solvent: toluene.

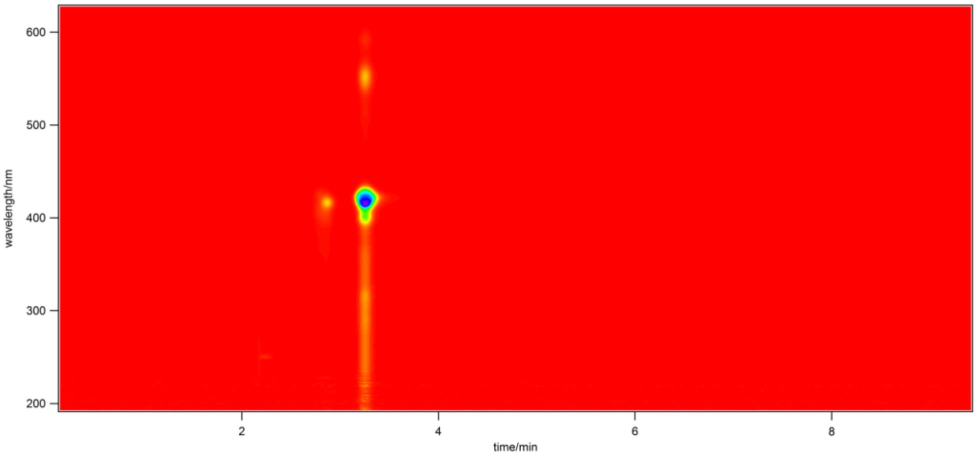

Figure S34 HPLC of ZnTPP. Solvent and mobile phase: EtOAc/(heptane+ EtOAc) = 0.15.

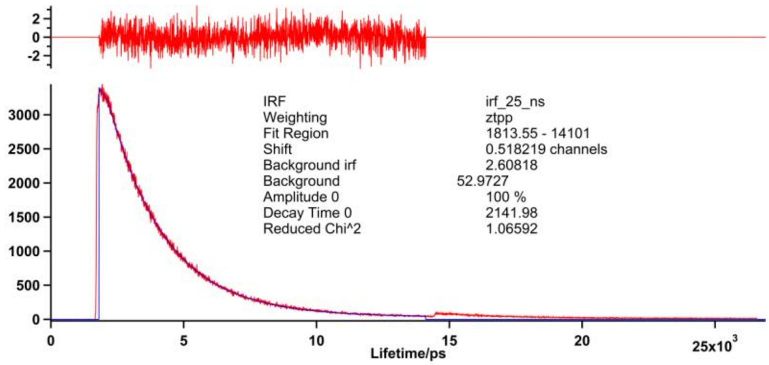

Figure S35 Fluorescence decay of ZnTPP in toluene (λ_{ex} = 400 nm, λ_{em}= 600 nm). The fitted lifetime (2.14 ns) agrees with the literature (2.06 ns).[7]

Rhodamine 101

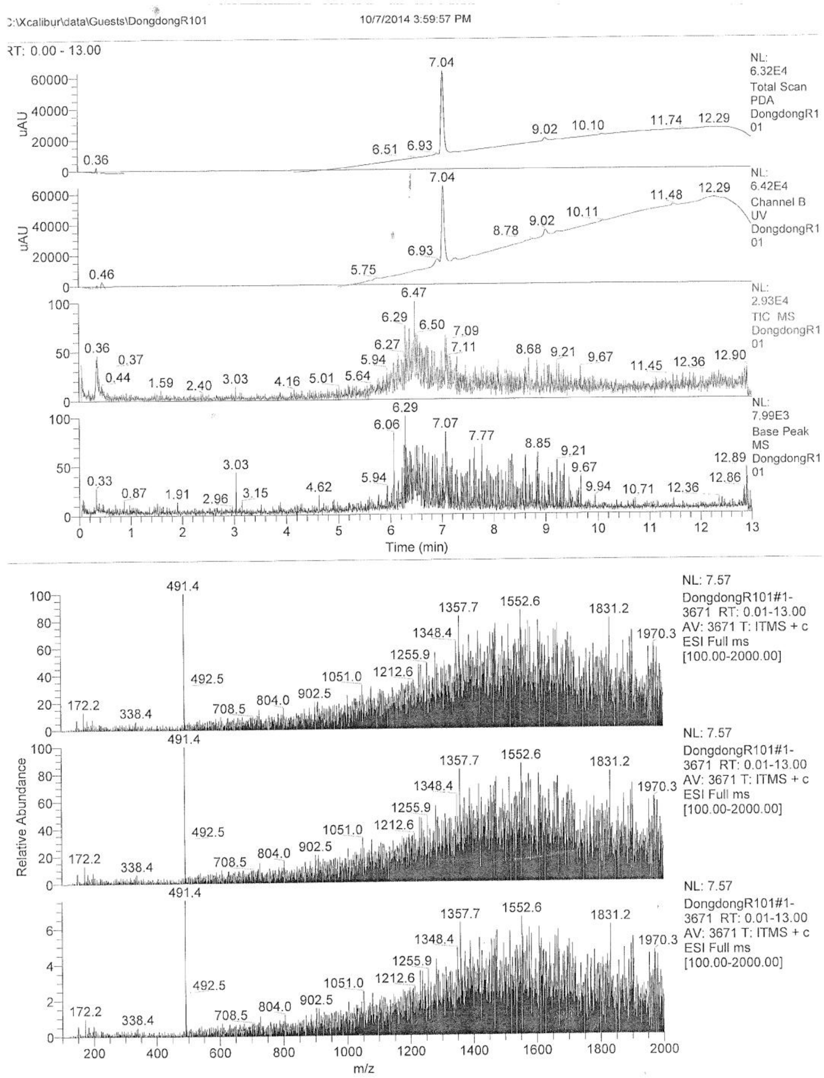

Figure S36 LCMS of R101. Solvent and mobile phase: MeCN:H_2O=1:1. The UV absorption trace reveals some impurities, but these may not affect the absorption and emission in the visible range.

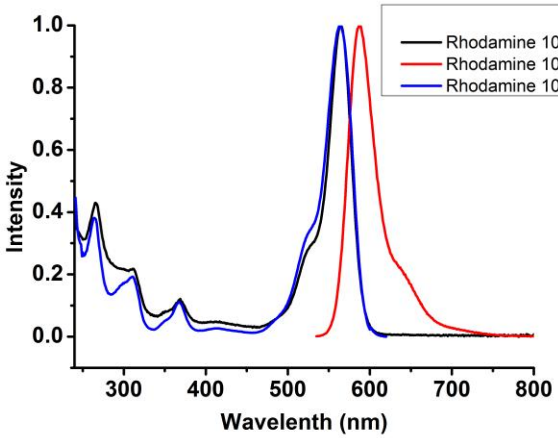

Figure S37 Normalized excitation (λ_{em} = 625 nm), emission (λ_{ex} = 510 nm), and absorption spectrum of R101. Solvent: EtOH.

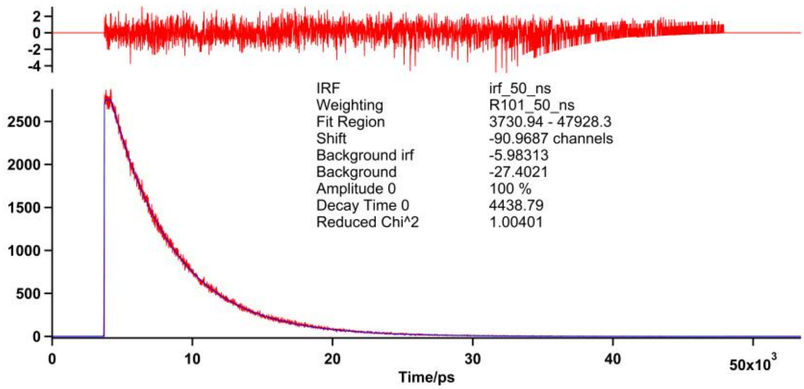

Figure S38 Fluorescence decay of Rhodamine 101 in EtOH (λ_{ex} = 488 nm, λ_{em} = 580 nm). The fitted lifetime (4.44 ns) is in agreement with the literature (4.6 ns).[8]

perylene red

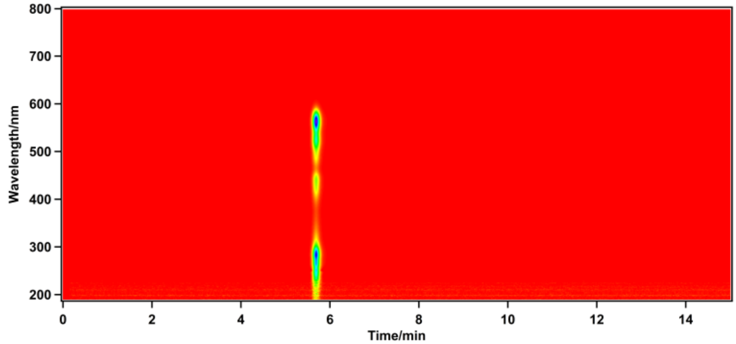

Figure S39 HPLC of perylene red. Solvent and mobile phase: EtOAc/(heptane+ EtOAc) = 0.15.

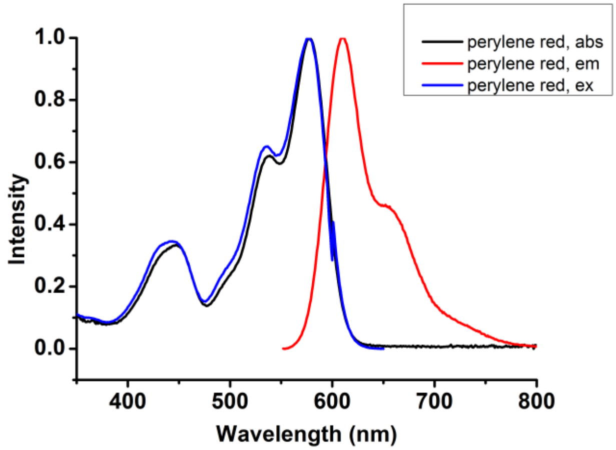

Figure S40 Normalized excitation (λ_{em} = 625 nm), emission (λ_{ex} = 510 nm), and absorption spectrum of perylene red. Solvent: chloroform.

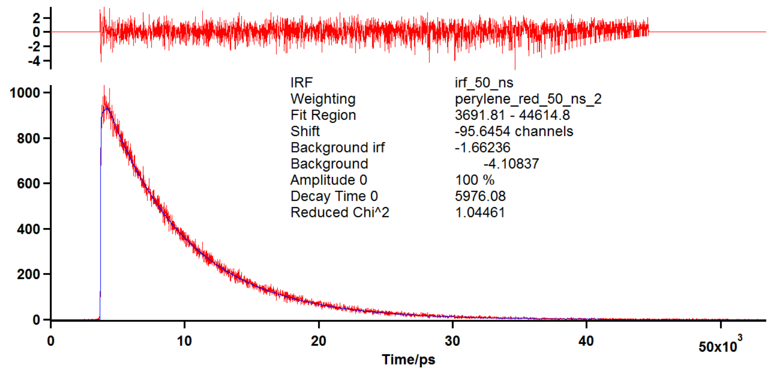

Figure S41 Fluorescence decay of perylene red in chloroform (λ_{ex} = 488 nm, λ_{em} = 602 nm). The fitted lifetime (5.98 ns) is shorter than the literature value (7.4 ns).[9] The reason for this is unknown.

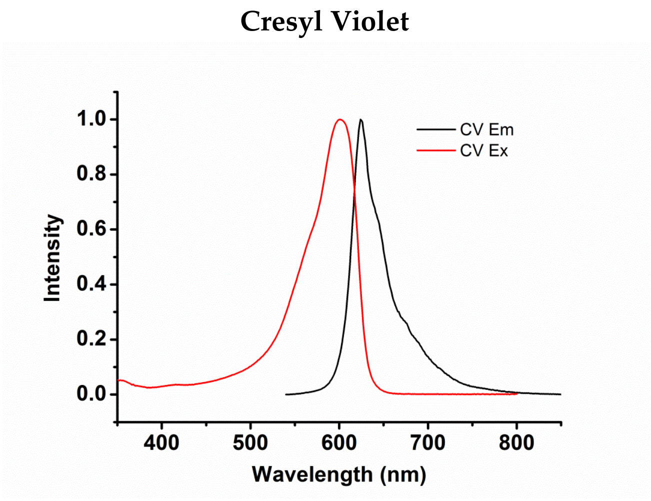

Figure S42 Normalized emission (λ_{ex} = 530 nm) and absorption spectra of Cresyl Violet. Solvent: EtOH.

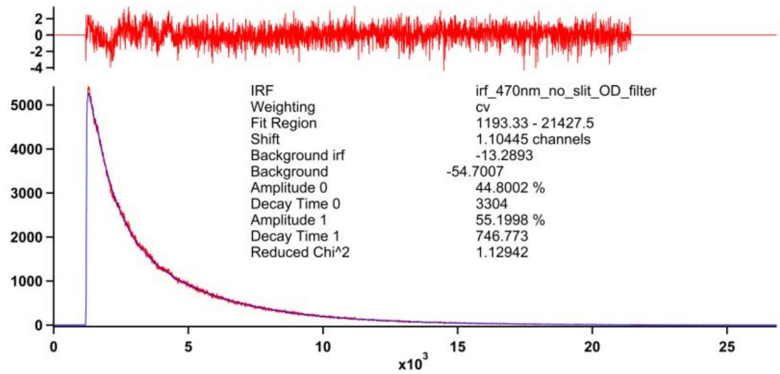

Figure S43 Fluorescence decay of CV in EtOH (λ_{ex} = 470 nm, λ_{em} = 630 nm). The decay is biexponential (45% 3.3 ns and 55% 0.75 ns), which is unexpected, and may be due to heterogeneity due to aggregation or deprotonation. According to the literature the decay is single-exponential (2.0 ns in water).[10]

Oxazine 1

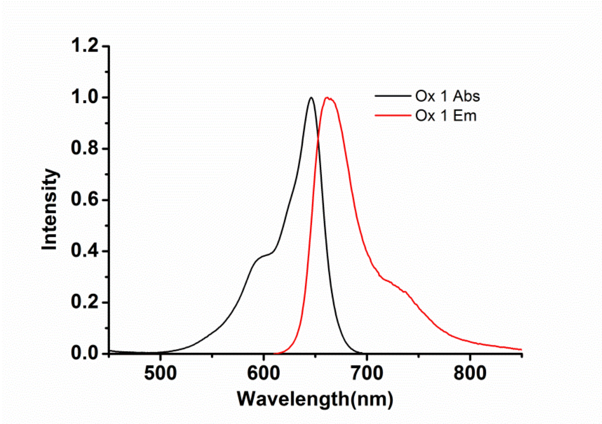

Figure S44 Normalized absorption and emission (λ_{ex} = 600 nm) spectra of Oxazine 1 in EtOH.

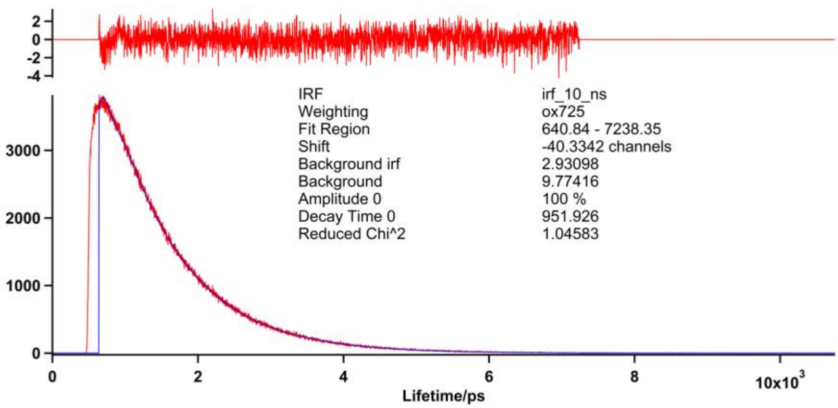

Figure S45 Fluorescence decay of Ox1 in toluene (λ_{ex} = 605 nm, λ_{em} = 670 nm). The fitted lifetime (0.95 ns) is considerably longer than that in the literature (0.6 ns).[11] The reason for this is unknown.

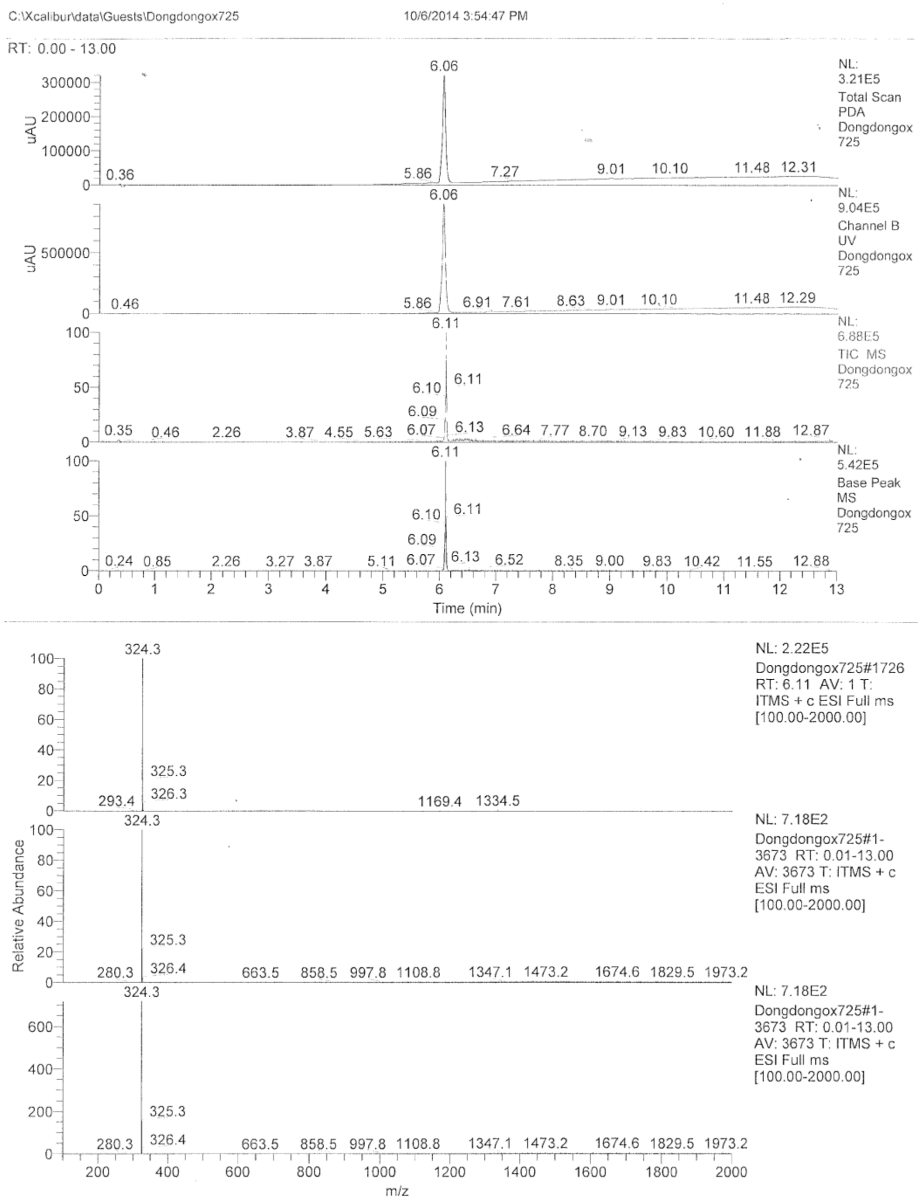

Figure S46 LCMS of Ox1. Solvent and mobile phase MeCN:H_2O=1:1.

Oxazine 170

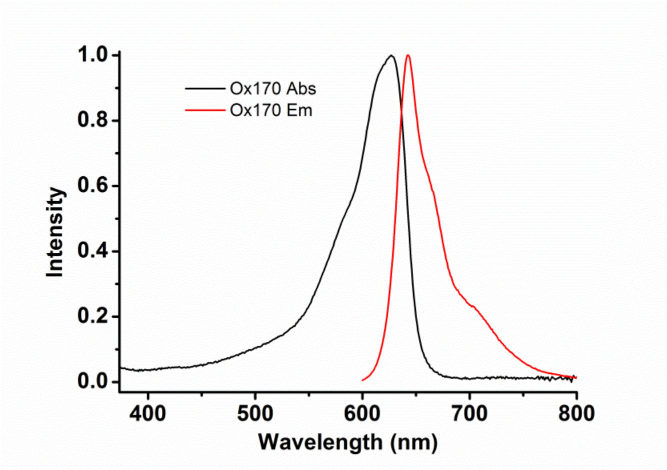

Figure S47 Normalized absorption and emission (λ_{ex} = 590 nm) spectrum of Oxazine 170. Solvent: EtOH.

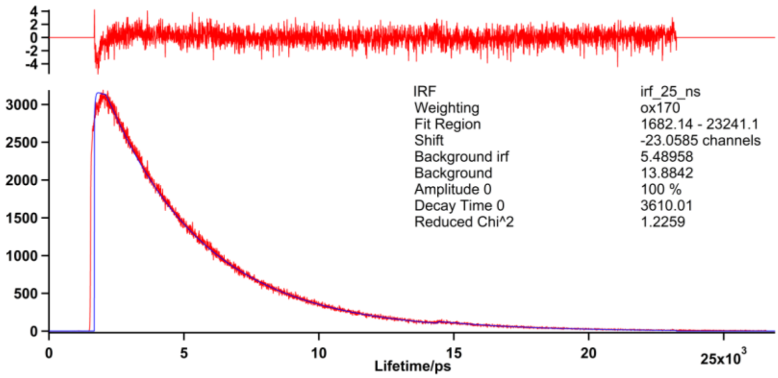

Figure S48 Fluorescence decay of Ox170 in EtOH (λ_{ex} = 605 nm, λ_{em} = 650 nm). The fitted lifetime (3.61 ns) does not agree very well with the literature (3.19 ns).[12] The fit is also not very good, indicating potential problems perhaps due to the presence of deprotonated species.

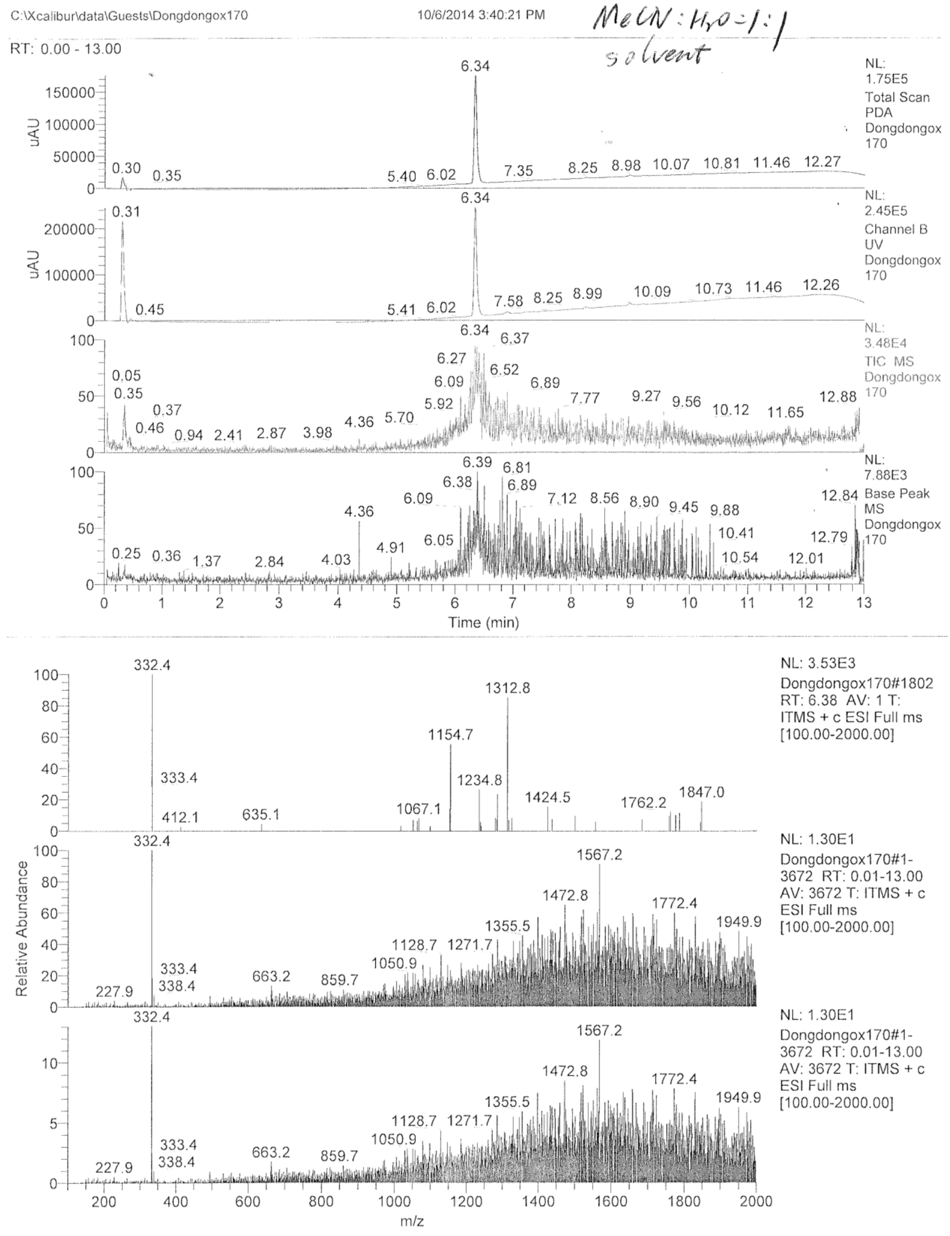

Figure S49 LCMS of Ox170. Solvent and mobile phase MeCN:H_2O = 1:1.

Zn-phthalocyanine

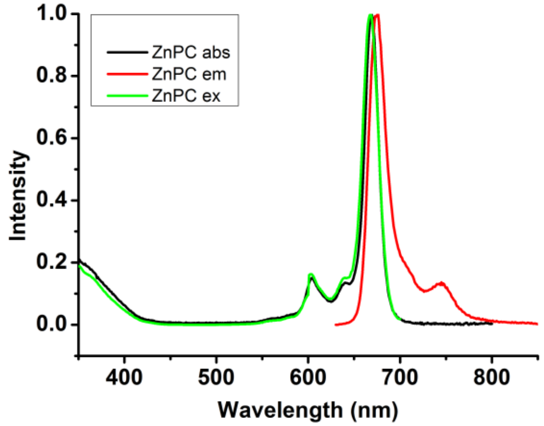

Figure S50 Normalized excitation (λ_{em} = 710 nm), emission (λ_{ex} = 610 nm), and absorption spectra of Zn-phthalocyanine in DMF.

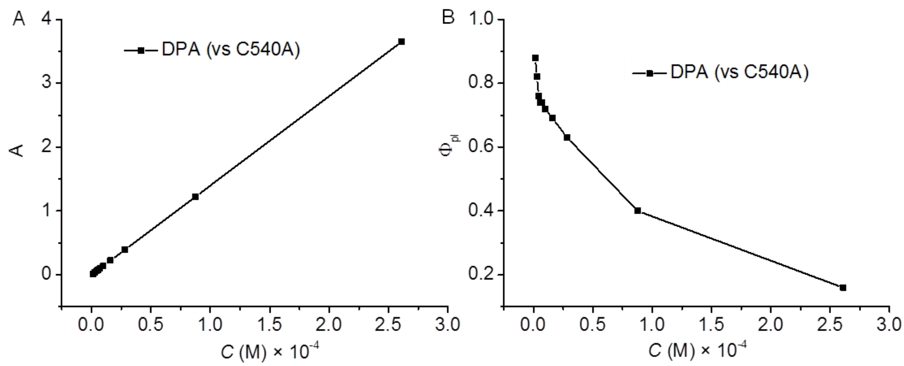

Figure S51 Absorption (A) and apparent quantum yield (B) of DPA in cyclohexane at different concentrations.

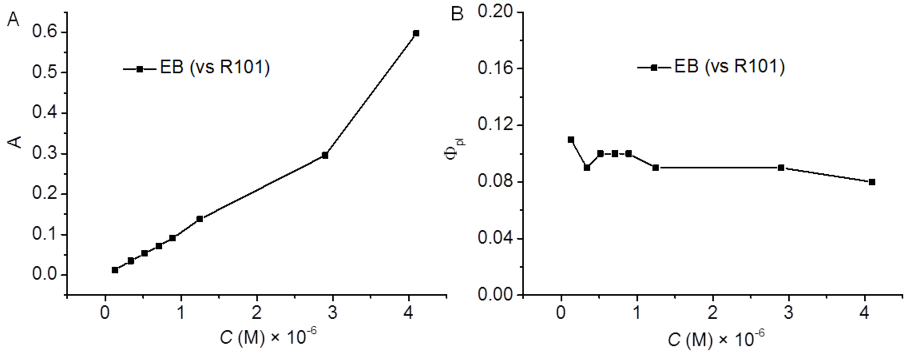

Figure S52 Absorption (A) and quantum yield (B) of Erythosine B in MeOH at different concentrations. Note: when the concentration of EB reaches 5.85 × 10^{-6} M, the growth of absorption intensity seems disproportionate to that of concentration, which maybe induced by dye aggregation.

References

1. N. Boens, W. Qin, N. Basaric, J. Hofkens, M. Ameloot, J. Pouget, J.-P. Lefevre, B. Valeur, E. Gratton, M. vandeVen, N. D. Silva, Jr., Y. Engelborghs, K. Willaert, A. Sillen, G. Rumbles, D. Phillips, A. J. W. G. Visser, A. van Hoek, J. R. Lakowicz, H. Malak, I. Gryczynski, A. G. Szabo, D. T. Krajcarski, N. Tamai and A. Miura, *Anal. Chem.*, 2007, **79**, 2137-2149.
2. C. J. Rocha, M. H. Gehlen, R. da Silva and P. M. Donate, *Journal of Photochemistry and Photobiology A: Chemistry*, 1999, **123**, 129-136.
3. M. Y. Berezin and S. Achilefu, *Chem. Rev.*, 2010, **110**, 2641-2684.
4. C. Würth, D. Geißler, T. Behnke, M. Kaiser and U. Resch-Genger, *Anal. Bioanal. Chem.*, 2015, **407**, 59-78.
5. P. K. Sharma, *Polymeric thin films for integrated optics*, PhD thesis, Durham University, 1992.
6. N. Boens, W. Qin, N. Basarić, J. Hofkens, M. Ameloot, J. Pouget, J.-P. Lefèvre, B. Valeur, E. Gratton and M. Vandeven, *Anal. Chem.*, 2007, **79**, 2137-2149.
7. D. Kowalska and R. P. Steer, *Journal of Photochemistry and Photobiology A: Chemistry*, 2008, **195**, 223-227.
8. D. Magde, G. E. Rojas and P. G. Seybold, *Photochem. Photobiol.*, 1999, **70**, 737-744.
9. F. Würthner, *Chem. Commun.*, 2004, 1564-1579.
10. P. Myslinski, D. Wieczorek and K. Kownacki, *Chem. Phys. Lett.*, 1989, **155**, 256-261.
11. F. Laermer, T. Elsaesser and W. Kaiser, *Chem. Phys. Lett.*, 1989, **156**, 381-386.
12. A. Grofcsik and W. J. Jones, *J. Chem. Soc., Faraday Trans.*, 1992, **88**, 1101-1106.