ELECTRONIC SUPPLEMENTARY INFORMATION

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Materials and Methods

The host octaacid (OA) and the guests were synthesized by following procedure previously published in the literature.[1] ^{1}H and ^{13}C NMR spectra (APT) were recorded on a Varian Inova 300 MHz spectrometer or Varian VNMRs 300 MHz spectrometer. The chemical shifts were expressed as δ (ppm) relative to tetramethylsilane (TMS) as the internal standard and using DMSO-d^6 (as the solvents) at room temperature. Data for ^{1}H NMR were reported as follows: multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), integration, coupling constant (Hz) and assignment Infrared spectra was recorded at 25°C on a Shimadzu Prestige 21 in ATR mode.

The ^{1}H NMR titration experiments were carried out on a Bruker 500 MHz NMR spectrometer at 25°C. A solution of the host Octa acid - 600 μL of a D_2O solution of OA (1 mM OA in 10 mM $Na_2B_4O_7$) - was taken in a NMR tube. To this solution an 0.25 equivalent increment of the guest was added (2.5 μL of a 60 mM solution in DMSO-d^6) up to the molar ratio 1:1 (H:G). The measurements were carried out after shaking the NMR tube for 2-5 min after each addition. The completion of complexation was monitored by disappearance of the free host octa acid signals upon the addition of the guest.

The 2:1 host-guest solution was prepared by adding 5.0 μL of 60 mM DMSO-d_6 solution of the guest to 0.6 mL of 1 mM OA in 10 mM $Na_2B_4O_7$ water solution and diluted using the latter $Na_2B_4O_7$ buffer depending on the need.

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1. (a) E. Ramasamy, N. Jayaraj, M. Porel and V. Ramamurthy, *Langmuir*, **2012**, *28*, 10. (b) E. Barni, P. Savarino, M. Marzona and M. Piva, *J. Heterocyclic Chem.*, **1983**, *20*, 1517. (c) T. Ozturk, A. S. Klymchenko, A. Capan, S. Oncul, S. Cikrikci, S. Taskiran, B. Tasan, F. B. Kaynak, S. Ozbey, A. P. Demchenko, *Tetrahedron*, **2007**, *63*, 10290.

For the photophysical study all the solvents and reagents were used as received or purified using standard procedures. Spectroscopic-grade solvents (Aldrich) were used for fluorescence and UV-Visible (UV-Vis) measurements. All experiments were performed at room temperature at a concentration of 10^{-5} M. UV-Vis absorption spectra were performed on a Shimadzu UV-2101PC spectrophotometer. Steady-state luminescence spectra were recorded using an Edinburgh Analytical Instruments FS920CDT fluorometer. Capsular assemblies of OA (1 mM) were made separately by adding 5 μL of 60 mM solution of guest (in DMSO-*d*^{6} solution) to 0.6 mL in 10 mM borate buffer in H_2O for a 2:1 (H:G) capsular assembly. These solutions were diluted using 10 mM borate buffer in H_2O. The quantum yield of fluorescence was measured at 25 °C using spectroscopic grade solvents within solutions with an absorbance intensity lower than 0.1 (optical dilute method).[2] Quinine sulfate (Riedel) in H_2SO_4 0.5 M was used as the quantum yield standard.[3]

Fluorescence lifetimes were measured by time-correlated single photon counting using a nF920 fluorometer (Edinburgh Analytical Instruments). As excitation source it was used EPLED-330 and EPLED-360. All measurements were performed at room temperature (25^{o}C). The fluorescence decay curves were analyzed using the software F900 (Analysis of Lifetime Data). A nonlinear least square method was employed for the fit of the decay to a sum of exponentials. The value of χ^2 and a visual inspection of the residuals and the autocorrelation function were used to determine the quality of the fit.

Spectroscopic data of the guests

2-(2'-hydroxyphenyl)benzoxazole (HBO)

White solid. Yield 60%. Melting point: 125-126 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm): 7.01 (t, 1H), 7.14 (d, 1H), 7.25 (m, 1H), 7.38 (m, 1H), 7.45 (t, 1H), 7.61 (m, 1H), 7.73 (m, 1H), 8.02 (d, 1H), 11.55 (broad s, 1H, OH).

3-hydroxyflavone (3HF)

White solid. Yield 28%. ^{1}H NMR (300 MHz, DMSO-*d*^{6}, TMS): δ (ppm): 7.37-7.56 (m, 4H), 7.67-7.79 (m, 2H), 8.07 (dd, 1H, J_o = 8.22 Hz and J_m = 1.76), 8.16 (dd, 2H, J_o = 8.22 Hz and J_m = 1.76 Hz), 9.55 (broad s, 1H, OH). ^{13}C NMR (75.4 MHz; DMSO-*d*^{6}): δ (ppm): 118.8, 121.7, 124.9, 125.2, 128.1, 128.9, 130.3, 131.7, 134.1, 139.5, 145.6, 155.0, 173.4. FTIR (ATR, cm^{-1}): 3212, 3071, 3056, 3031, 3018, 1610.

2. C. Würth, M. Grabolle, J. Pauli, M. Spieles, U. Resch-Genger, *Nat. Protoc*., **2013**, *8*, 1535.

3. (a) J. N. Demas, G. A. Crosby, *J. Phys. Chem*., **1971**, *75*, 991. (b) S. Fery-Forgues, D. J. Lavabre, *J. Chem. Educ*., **1999**, *76*, 1260.

Photoinduced electron transfer (PET) experiment

Steady-state and time-resolved fluorescence studies were performed using: [4]

3HF experiment: Stock solutions of 3HF@$(OA)_2$ at a concentration of $29.4x10^{-5}$ M, MV^{+2} or MP^{+} at a concentration of $4.75x10^{-3}$ M, diluted in stock solution of 3HF@$(OA)_2$

HBO experiment: HBO@$(OA)_2$ at a concentration of $1.56x10^{-5}$ M, MV^{+2} or MP^{+} at a concentration of $2.35x10^{-3}$ M, diluted in HBO@$(OA)_2$

For PET experiments, the MV^{+2} or MP^{+} stock solution was added dropwise to the 3HF or HBO solution, until no further change in the emission spectra was observed. To the measurements, 1.5 mL of 3HF or HBO stock solution was added in a cuvette and added 1.0, 4.0, 7.0, 10.0, 15.0 and 20.0 μL of the respective MV^{+2} or MP^{+} stock solution, as presented in Table ESI1..

Table ESI1. Working concentrations used to the PET experiment.

Compound	Solvent	Concentration (M)	Amount (μL)
3HF@$(OA)_2$	Buffer[a]	$2.94x10^{-5}$	-
MV^{+2} MP^{+}	3HF@$(OA)_2$ solution[b]	$4.75x10^{-3}$	1.0, 4.0, 7.0, 10.0, 15.0, 20.0 (and 30.0)[e]
HBO@$(OA)_2$	Buffer[a]	$1.56x10^{-5}$	-
MV^{+2} MP^{+}	HBO@$(OA)_2$ solution[b]	$2.35x10^{-3}$	1.0, 4.0, 7.0, 10.0, 15.0 and 20.0
Cucurbit[7]uril (CB7)	Buffer[a]	$23.2x10^{-4}$[c] 35.610^{-4}[d]	20.0

[a]Sodium tetraborate in water [10 mM]. [b]10 mM $Na_2B_4O_7$ solution. [c]added to the final solution of [3HF@$(OA)_2$]/[MV^{+2}] as complexing agent to the electron acceptor. [d]added to the final solution of [HBO@$(OA)_2$]/[MV^{+2}] as complexing agent to the electron acceptor. [e]only for [3HF@$(OA)_2$]/[MP^{+}].

Photophysics data

4. The electron acceptor (MV^{+2} or MP^{+}) stock solutions were made by its dilution in donor stock solutions to certificate no changes in donor concentration while doing titration experiments.

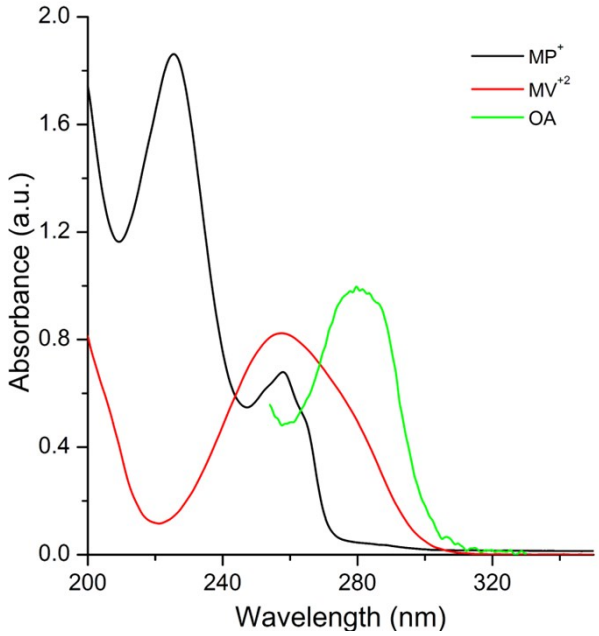


Fig. ESI1 Absorption spectra of electron acceptors MP^{+}, MV^{+2} and supramolecular host octaacid (OA) in 10 mM tetraborate buffer in absence of the ESIPT dyes. $[MP^{+}]=2.62x10^{-4}$ M, $[MV^{+2}]=6.29x10^{-4}$ M and $[OA]=1.00x10^{-3}$ M.

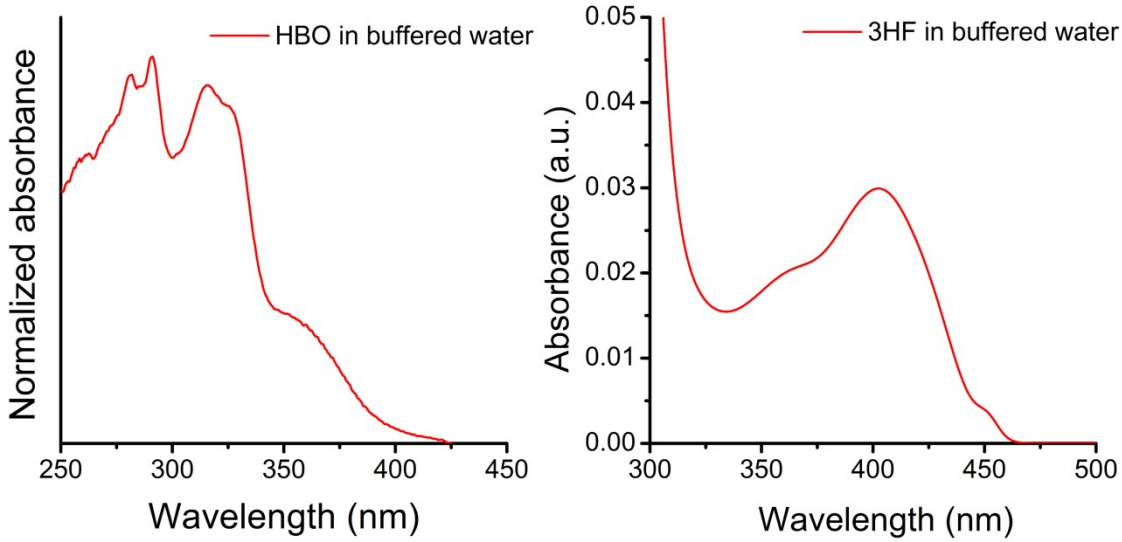


Fig. ESI2 Absorption spectra of HBO and 3HF in 10 mM tetraborate buffer in absence of the ESIPT dyes. $[3HF]=10^{-7}$ M and $[HBO]=10^{-6}$ M.

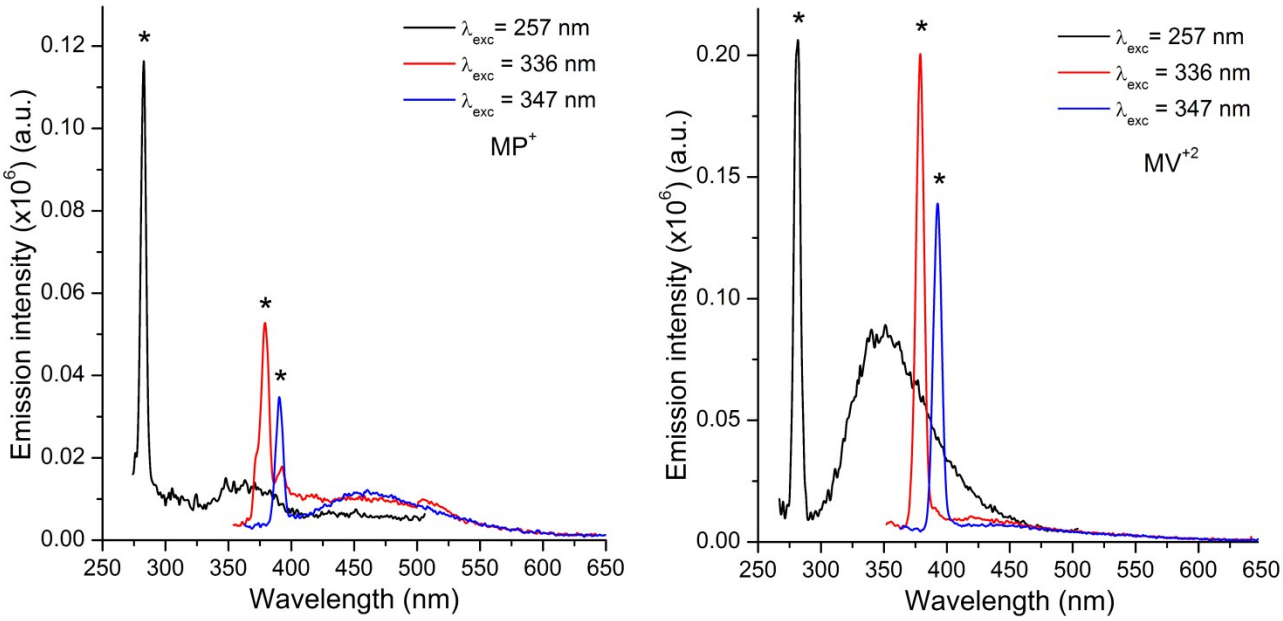


Fig. ESI3 Fluorescence emission spectra of electron acceptors MP^{+} (left) and MV^{+2} (right) in 10 mM tetraborate buffer in absence of the ESIPT dyes. $[MP^{+}]=2.62X10^{-4}$ M and $[MV^{+2}]=6.29x10^{-4}$ M. The asterisk indicates the scattering signal from the excitation wavelengths.

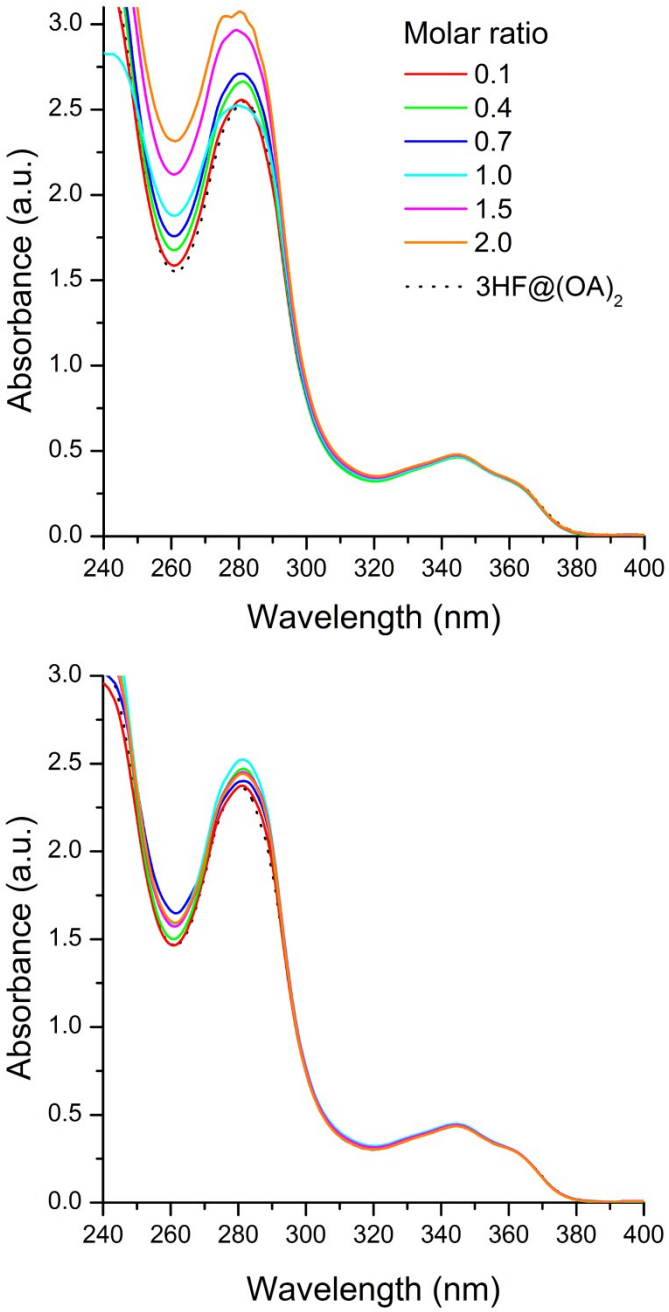


Fig. ESI4 UV-Vis absorption titration of 3HF@$(OA)_2$ in 10 mM sodium tetraborate buffer in presence of different amounts of MV^{+2} (top) and MP^{+} (bottom) (1.0-20.0 μL). Working concentrations [3HF@$(OA)_2$]: 2.94x10^{-5} M, [MV^{+2}] and [MP^{+}]: 4.75x10^{-3} M.

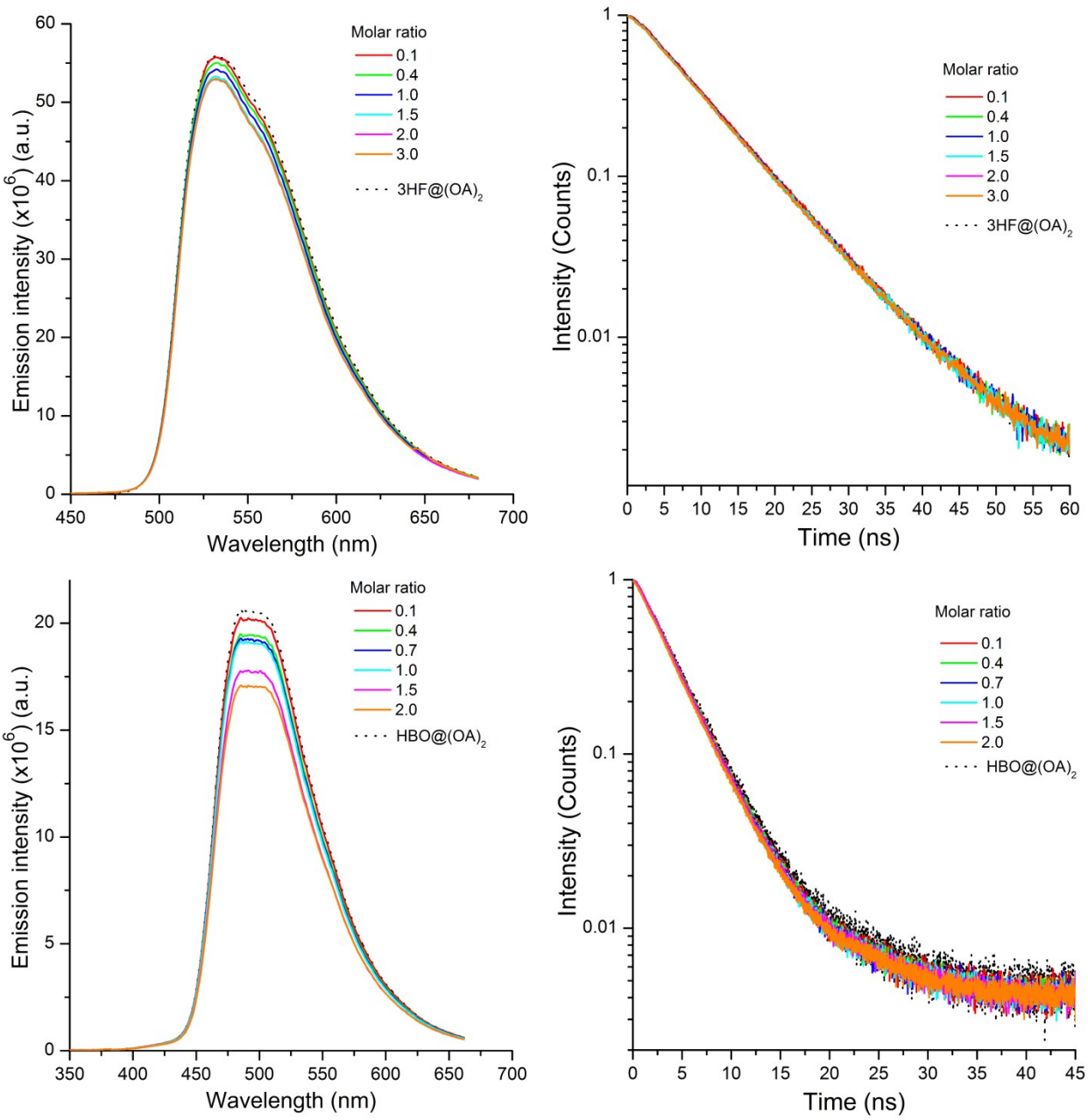


Fig. ESI5 Fluorescence titration spectra (left) and normalized fluorescence lifetime curves (right) of $3HF@(OA)_2$ and $HBO@(OA)_2$ in presence of different amounts of MP^+. Working concentrations $[HBO@(OA)_2]$: $1.56x10^{-5}$ M, $[3HF@(OA)_2]$: $2.94x10^{-5}$ M and $[MP^+]$: $4.75x10^{-3}$ M. Molar ratio $[MP^+]/[ESIPT@(OA)_2]$. The $3HF@(OA)_2$ and $HBO@(OA)_2$ are also presented in absence of the electron acceptor for comparison.

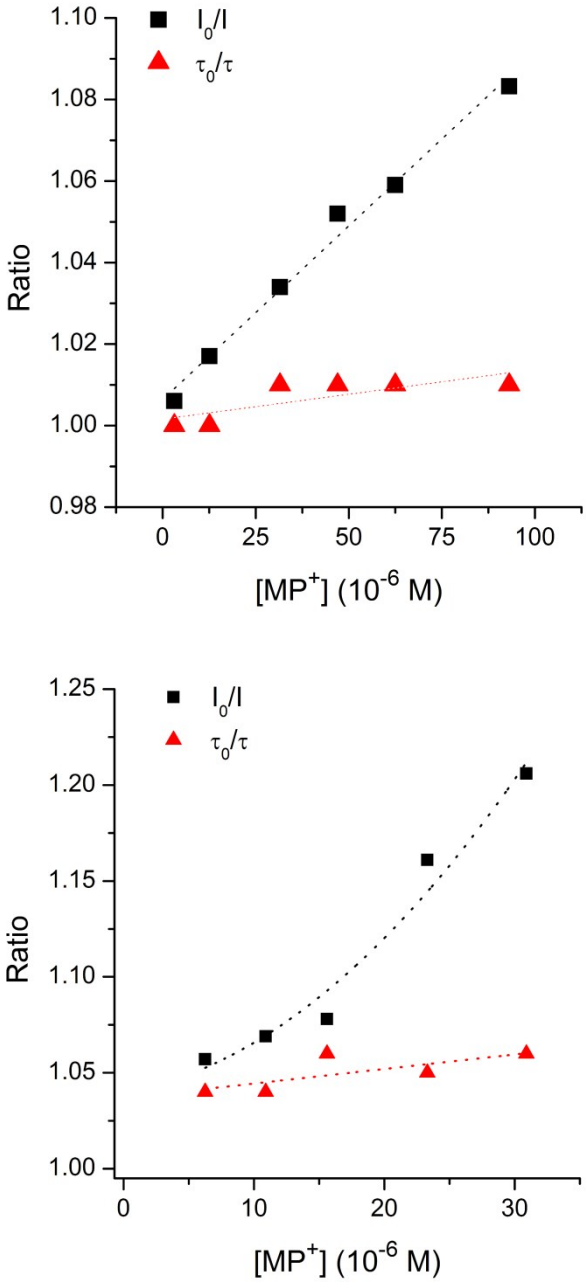


Fig. ESI6 Stern-Volmer plot of $3HF@(OA)_2$ (top) and $HBO@(OA)_2$ (bottom) in presence of different amounts of MP^+. Working concentrations [$HBO@(OA)_2$]: $1.56x10^{-5}$ M, [$3HF@(OA)_2$]: $2.94x10^{-5}$ M and [MP^+]: $4.75x10^{-3}$ M.

Table ESI2. Working concentrations (x10^{-6} M) of the electron donors HBO@$(OA)_2$ and 3HF@$(OA)_2$ with the electron acceptor MV^{+2}, fluorescence intensity and fluorescence lifetime ratios, I_0/I and τ_0/τ, respectively to Stern-Volmer plot.

System	Molar Ratio	[HBO@OA_2]	[MV^{+2}]	I_0/I	τ_0/τ
	0		0	1.000	1.000
	0.1		1.57	1.157	1.021
	0.4		6.25	1.265	1.035
[MV^{+2}]/[HBO@$(OA)_2$]	0.7	15.6	10.9	1.299	1.047
	1.0		15.6	1.378	1.060
	1.5		23.3	1.714	1.082
	2.0		30.9	2.143	1.093
System	**Molar Ratio**	**[3HF@OA_2]**	**[MV^{+2}]**		
	0		0	1.000	1.000
	0.1		3.16	1.012	1.013
	0.4		12.6	1.072	1.025
[MV^{+2}]/[3HF@$(OA)_2$]	0.7	29.4	22.1	1.134	0.966
	1.0		31.5	1.229	0.974
	1.5		47.0	1.346	0.984
	2.0		62.5	1.486	0.999

Table ESI3. Working concentrations of the electron donors HBO@$(OA)_2$ and 3HF@$(OA)_2$ with the electron acceptor MP^+, fluorescence intensity and fluorescence lifetime ratios, I_0/I and τ_0/τ, respectively to Stern-Volmer plot.

System	Molar Ratio	[HBO@OA_2]	[MP^+]	I_0/I	τ_0/τ
	0		0	1.000	1.000
	0.1		1.57	1.018	1.038
	0.4		6.25	1.057	1.041
[MP^+]/[HBO@$(OA)_2$]	0.7	15.6	10.9	1.069	1.047
	1.0		15.6	1.078	1.056
	1.5		23.3	1.161	1.054
	2.0		30.9	1.206	1.057
System	**Molar Ratio**	**[3HF@OA_2]**	**[MP^+]**		
	0		0	1.000	1.000
	0.1		3.16	1.006	1.000
	0.4		12.6	1.017	1.003
[MP^+]/[3HF@$(OA)_2$]	1.0	29.4	31.5	1.034	1.006
	1.5		47.0	1.052	1.006
	2.0		62.5	1.059	1.006
	3.0		93.1	1.058	1.007

Table ESI4. Relevant data from the time resolved fluorescence spectroscopy from 3HF@$(OA)_2$ inclusion complexes,[a] B is the pre-exponential factor, τ is the fluorescence lifetime (in ns), *Rel.* is relative contribution (in %) and χ^2 is the chi-square of the fit.

System	Molar Ratio	A	B_1	τ_1	Rel.	B_2	τ_2	Rel.	χ^2
$[MV^{+2}]$/[3HF@$(OA)_2$]	0	22.793	-	-	-	13560.423	8.3	100	1.093
	0.1	22.825	-	-	-	12662.848	8.2	100	1.099
	0.4	28.960	-	-	-	7937.069	8.1	100	1.137
	0.7	37.478	4748.053	5.2	16.66	14519.707	8.6	83.34	1.116
	1.0	30.866	9007.746	4.7	21.68	17897.311	8.5	78.32	1.078
	1.5	27.280	11613.523	4.1	26.01	16216.216	8.4	73.99	1.101
	2.0	43.502	20653.713	3.7	28.96	22647.094	8.3	71.04	1.090
$[MP^{+}]$/[3HF@$(OA)_2$]	0	39.762	-	-	-	21626.883	8.3		1.107
	0.1	37.908	-	-	-	19132.422	8.3		1.111
	0.4	38.007	-	-	-	19655.053	8.2	100	1.108
	1.0	38.370	-	-	-	21481.475	8.2		1.159
	2.0	36.867	-	-	-	19052.787	8.2		1.189
	3.0	39.765	-	-	-	19075.416	8.2		1.170

[a]Using an EPLED of 360 nm as excitation source and emission monitored at 533 nm.

Table ESI5. Relevant data from the time resolved fluorescence spectroscopy from HBO@$(OA)_2$ inclusion complexes,[a] B is the pre-exponential factor, τ is the fluorescence lifetime (in ns), *Rel.* is relative contribution (in %) and χ^2 is the chi-square of the fit.

System	Molar Ratio	A	B	τ	Rel.	χ^2
$[MV^{+2}]$/[HBO@$(OA)_2$]	0	26.933	4236.234	3.7		1.096
	0.1	37.786	6186.172	3.7		1.069
	0.4	44.666	7474.926	3.6		1.096
	0.7	64.669	10682.670	3.6	100	1.060
	1.0	72.012	12087.289	3.5		1.020
	1.5	65.128	10856.456	3.5		1.008
	2.0	70.485	10372.511	3.4		1.056
$[MP^{+}]$/[HBO@$(OA)_2$]	0	26.933	4236.234	3.7		1.096
	0.1	64.595	8714.659	3.6		1.108
	0.4	105.948	14388.769	3.6		1.082
	0.7	90.398	12278.782	3.6	100	1.102
	1.0	97.351	11146.600	3.6		1.106
	1.5	127.946	16549.121	3.6		1.109
	2.0	116.001	15357.481	3.5		1.108

[a]Using an EPLED of 330 nm as excitation source and emission monitored at 495 nm.

Time resolved fluorescence data

Titration data of [MV^{+2}]/[HBO@$(OA)_2$]

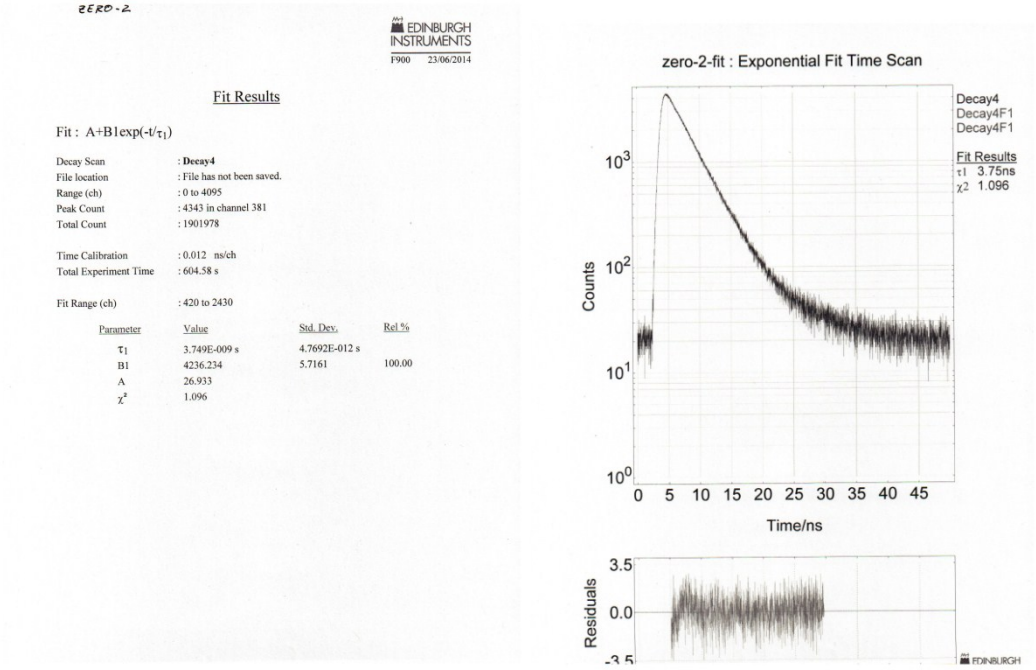


Fig. ESI7 Fit results of HBO@$(OA)_2$ (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

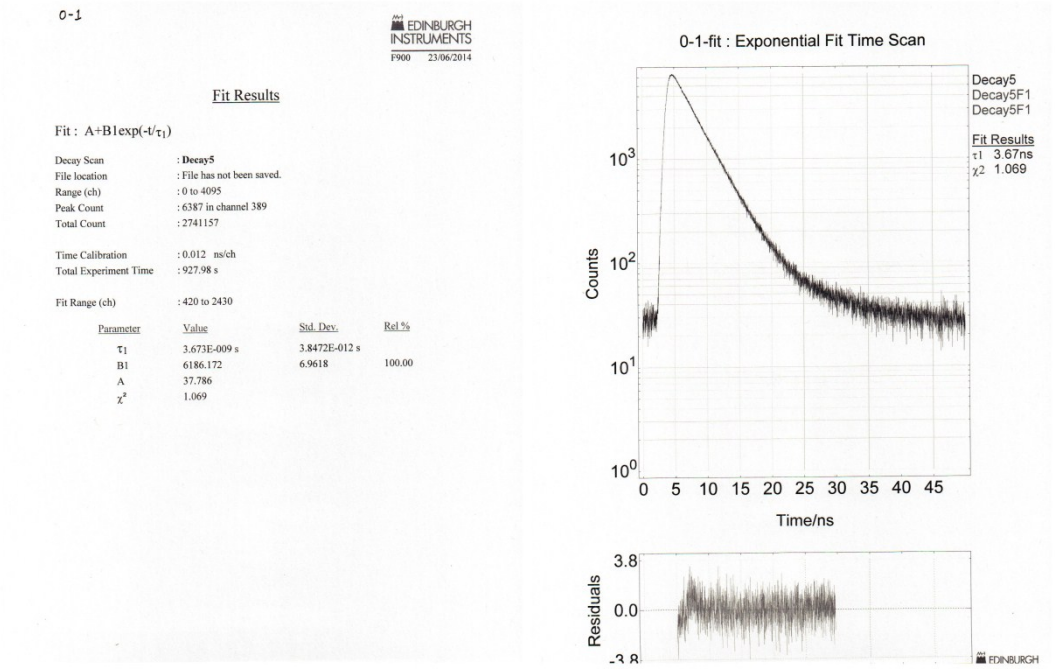


Fig. ESI8 Fit results of [MV^{+2}]/[HBO@$(OA)_2$] in a molar ratio of 0.1 (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

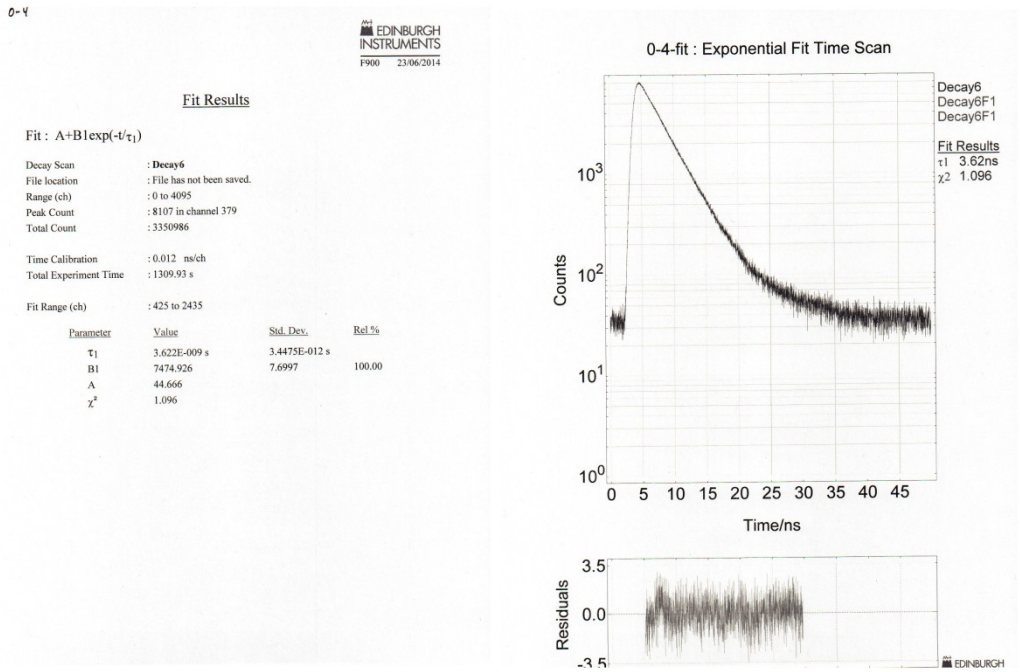


Fig. ESI9 Fit results of $[MV^{+2}]/[HBO@(OA)_2]$ in a molar ratio of 0.4 (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

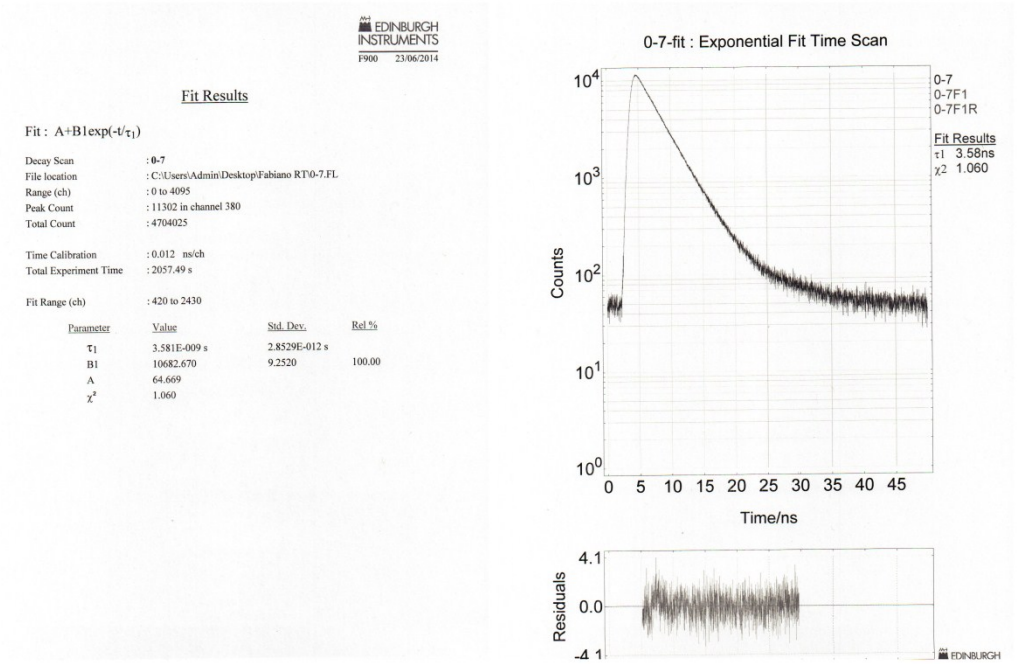


Fig. ESI10 Fit results of $[MV^{+2}]/[HBO@(OA)_2]$ in a molar ratio of 0.7 (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

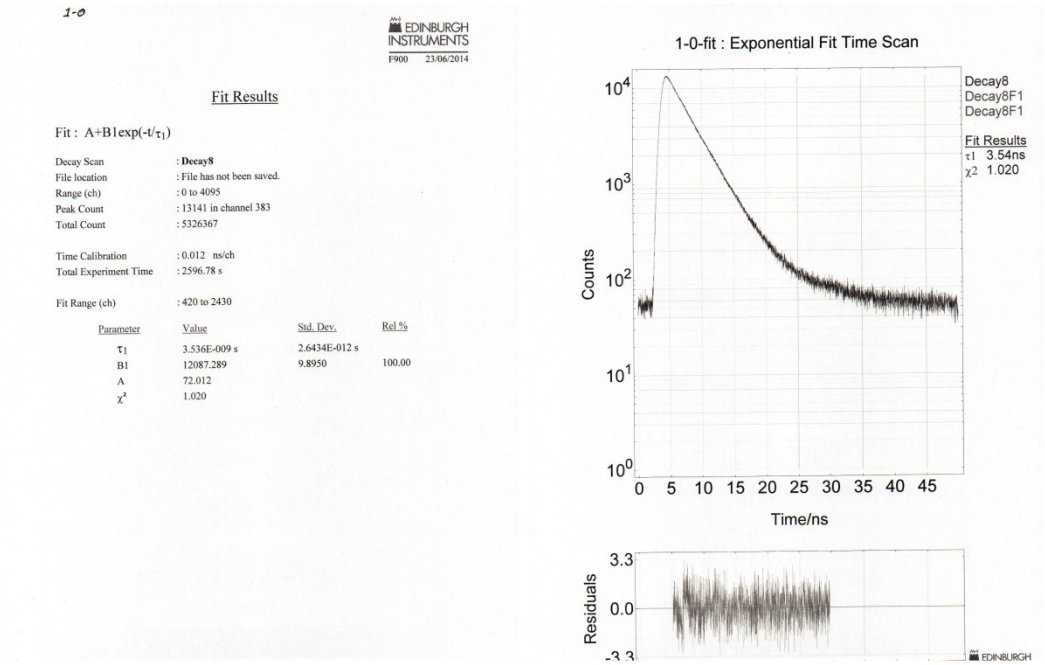


Fig. ESI11 Fit results of $[MV^{+2}]/[HBO@(OA)_2]$ in a molar ratio of 1.0 (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

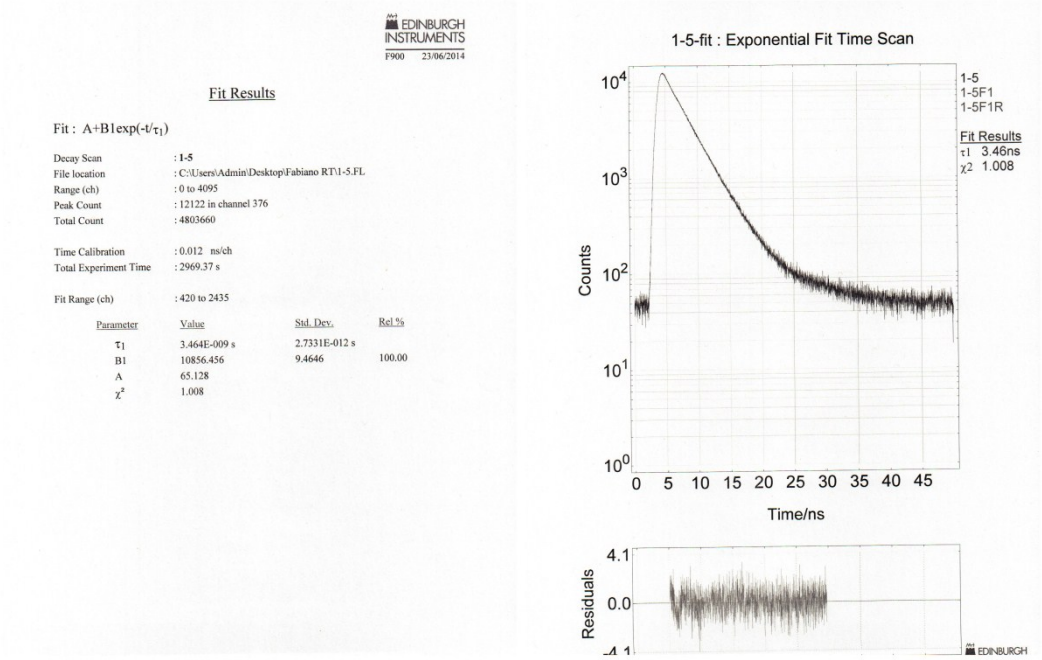


Fig. ESI12 Fit results of $[MV^{+2}]/[HBO@(OA)_2]$ in a molar ratio of 1.5 (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

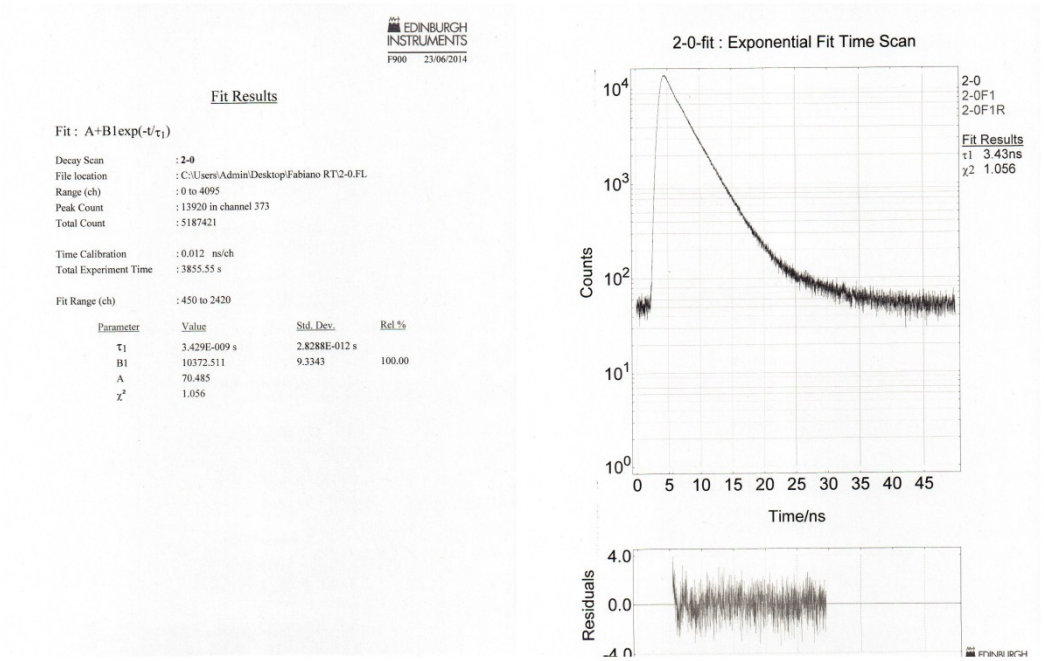


Fig. ESI13 Fit results of $[MV^{+2}]/[HBO@(OA)_2]$ in a molar ratio of 2.0 (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

Titration data of $[MP^{+}]/[HBO@(OA)_2]$

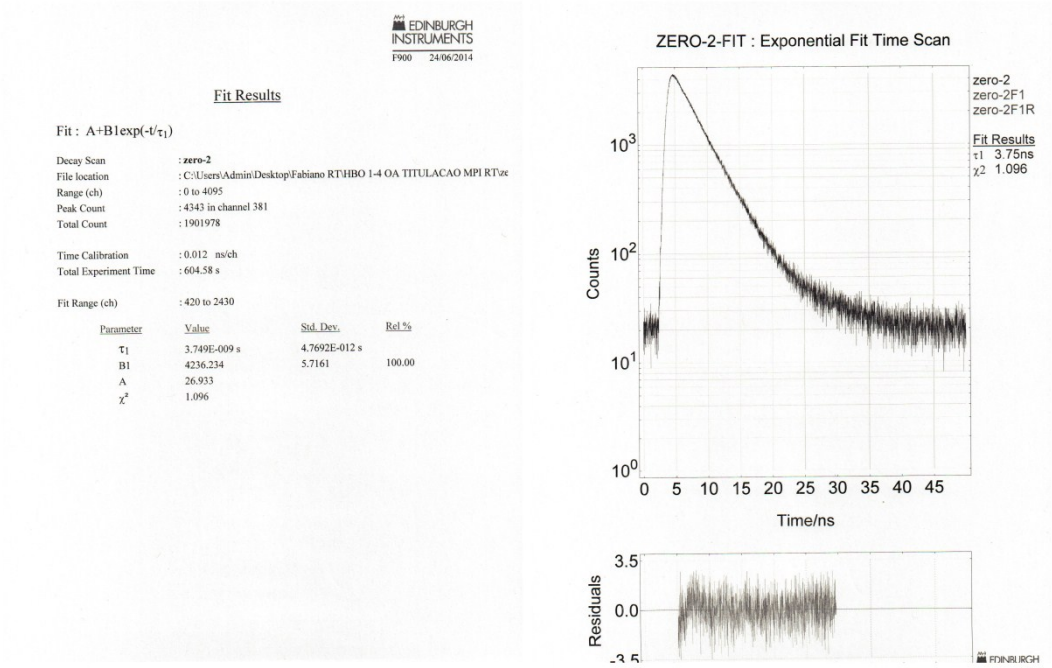


Fig. ESI14 Fit results of $HBO@(OA)_2$ (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

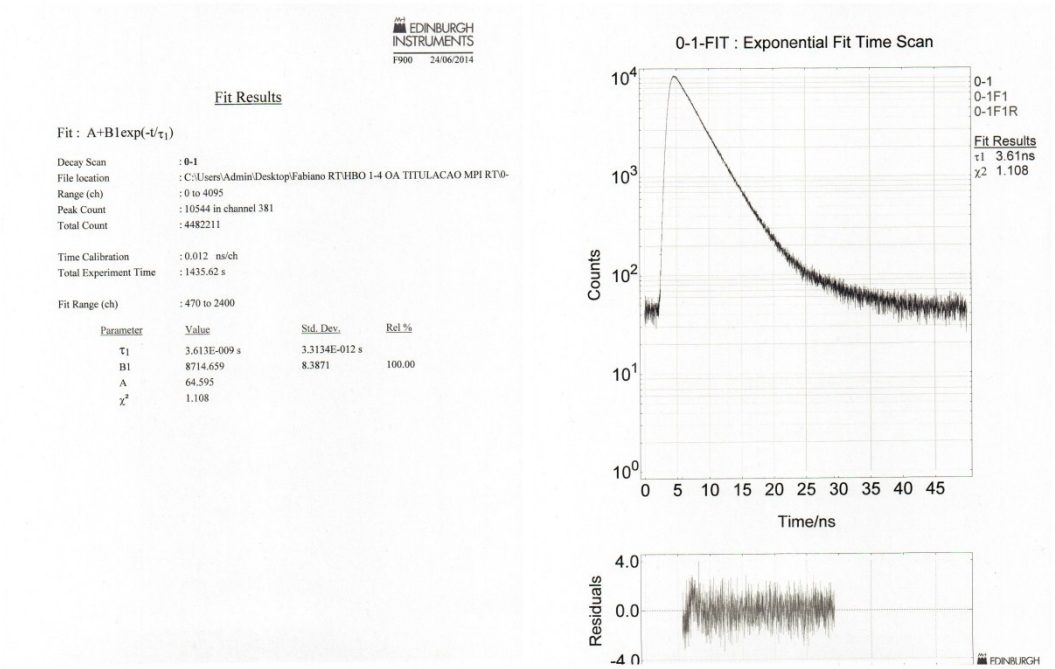


Fig. ESI15 Fit results of $[MP^+]/[HBO@(OA)_2]$ in a molar ratio of 0.1 (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

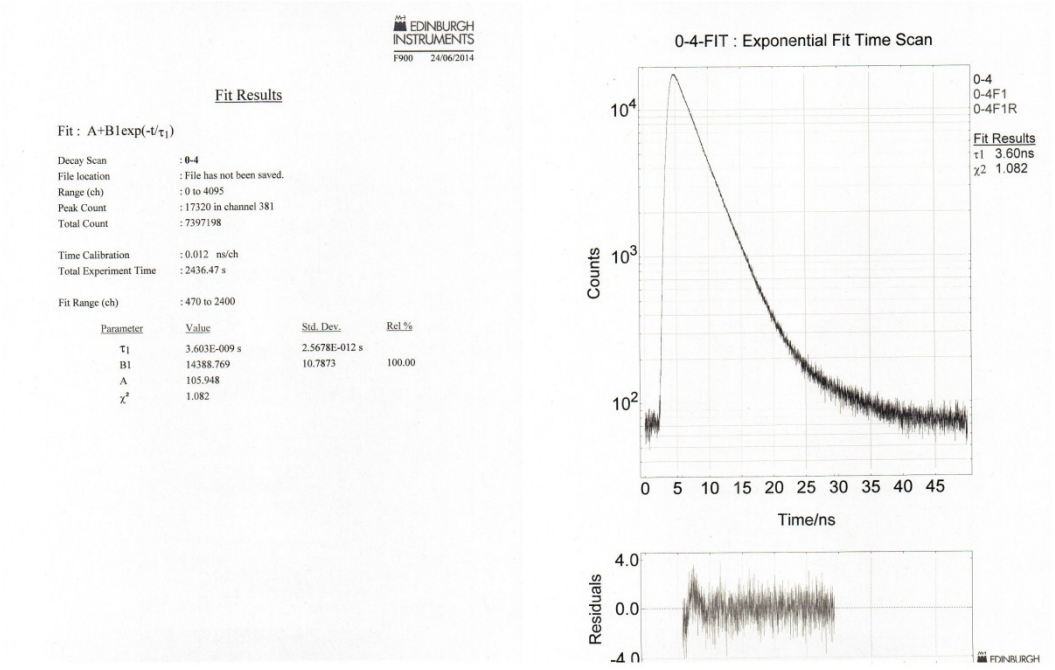


Fig. ESI16 Fit results of $[MP^+]/[HBO@(OA)_2]$ in a molar ratio of 0.4 (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

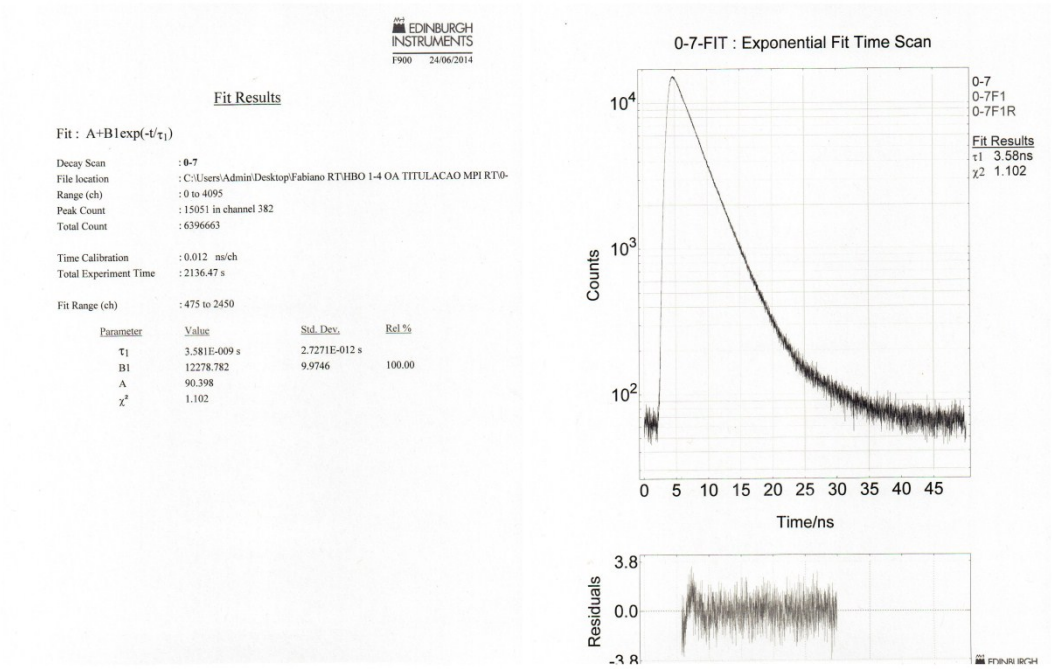


Fig. ESI17 Fit results of $[MP^+]/[HBO@(OA)_2]$ in a molar ratio of 0.7 (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

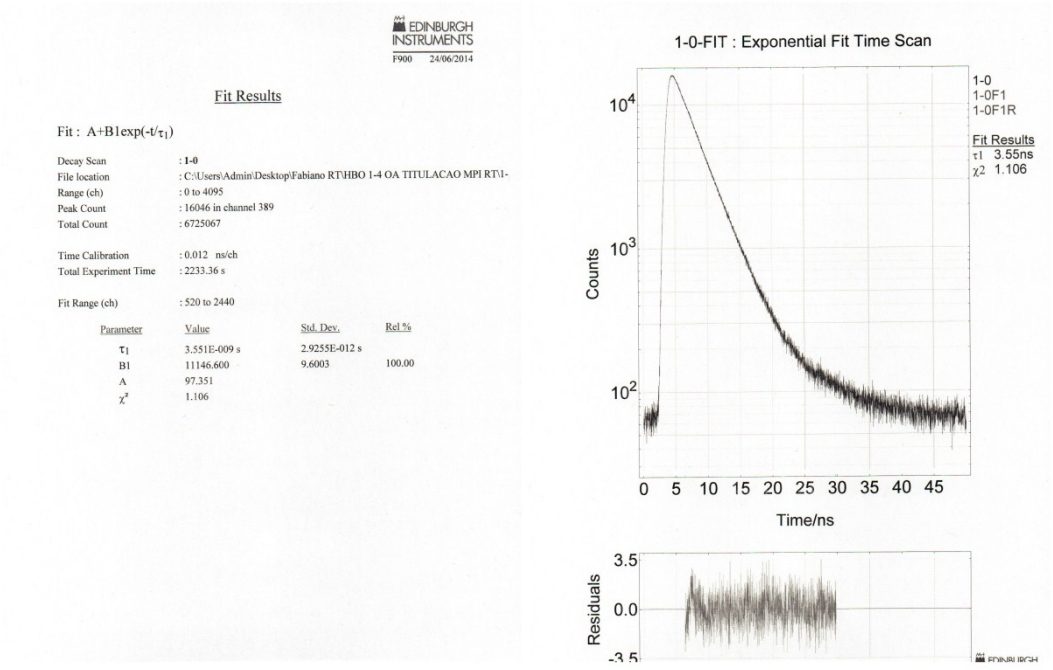


Fig. ESI18 Fit results of $[MP^+]/[HBO@(OA)_2]$ in a molar ratio of 1.0 (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

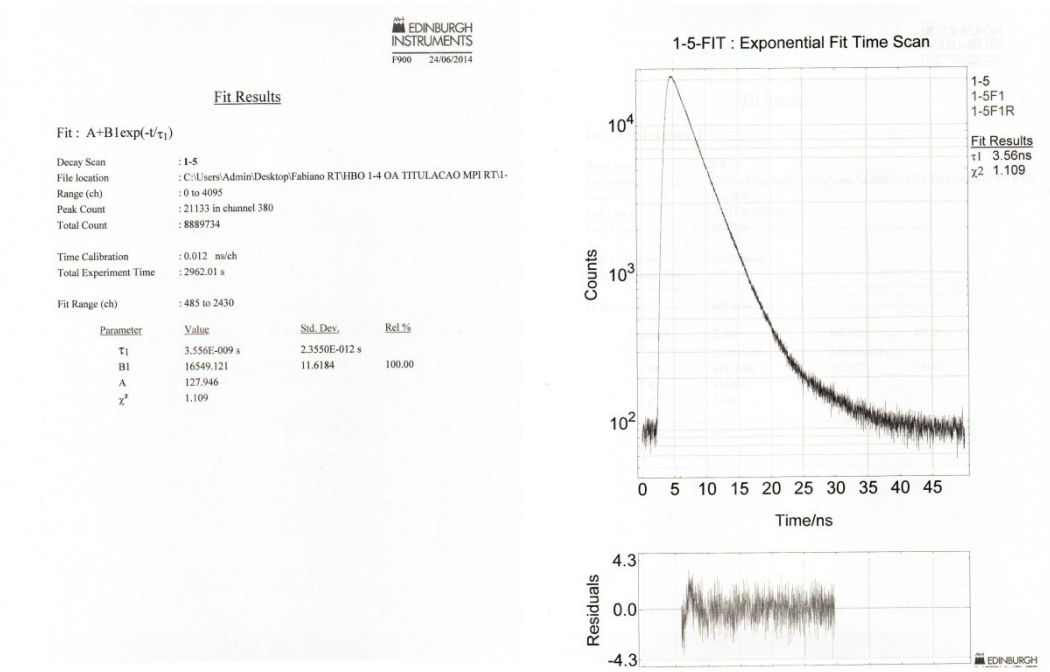


Fig. ESI19 Fit results of $[MP^+]/[HBO@(OA)_2]$ in a molar ratio of 1.5 (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

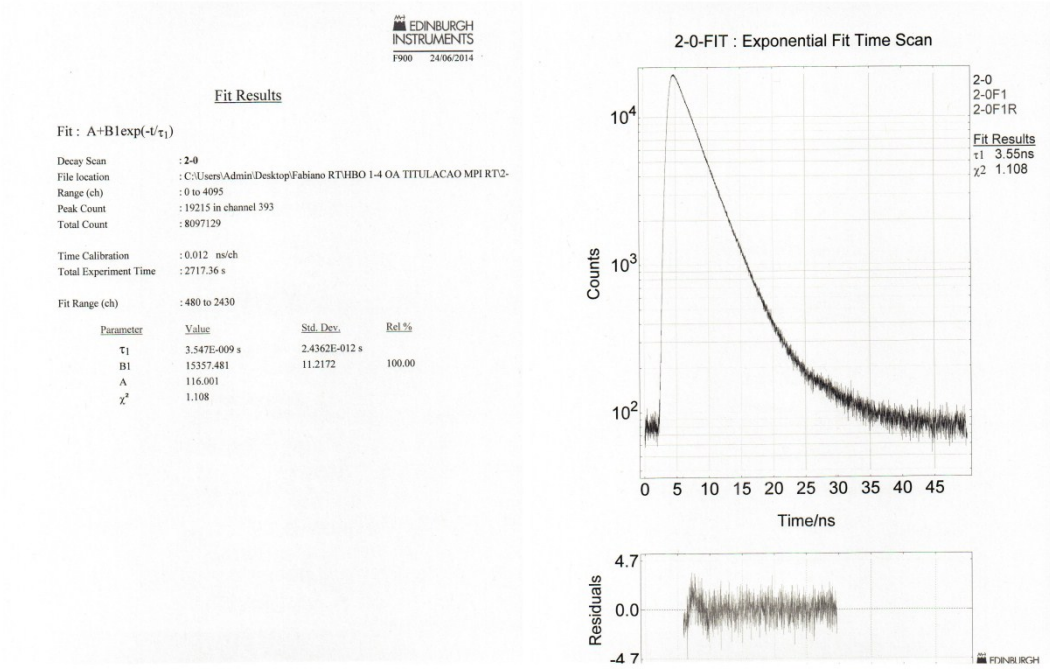


Fig. ESI20 Fit results of $[MP^+]/[HBO@(OA)_2]$ in a molar ratio of 2.0 (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

Titration data of [MV^{+2}]/[3HF@$(OA)_2$]

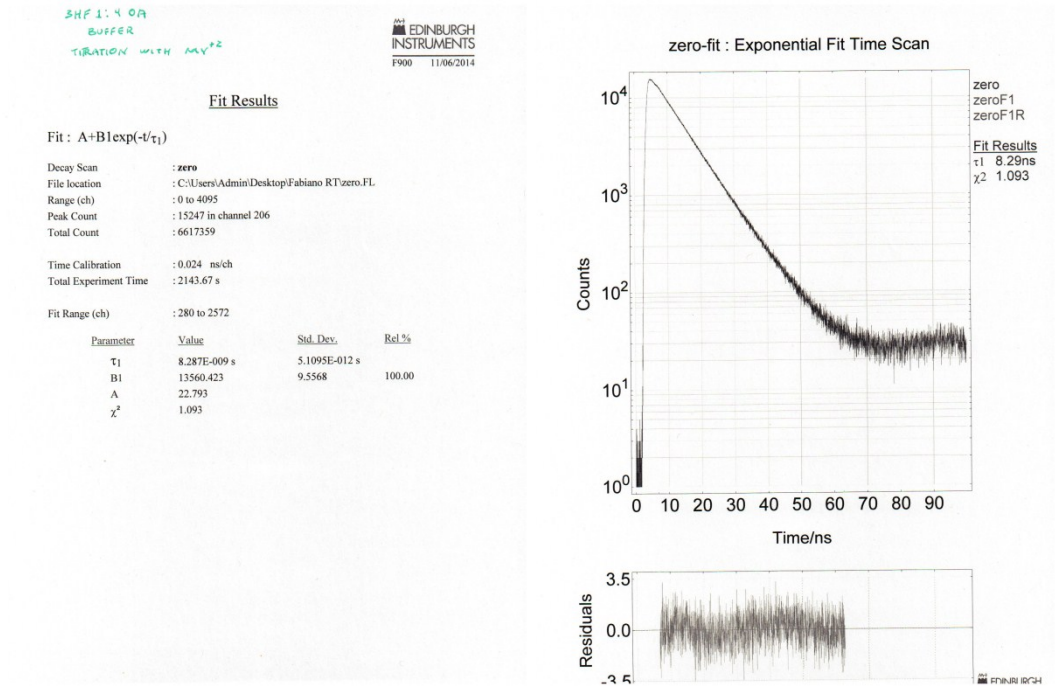


Fig. ESI21 Fit results of 3HF@$(OA)_2$ (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

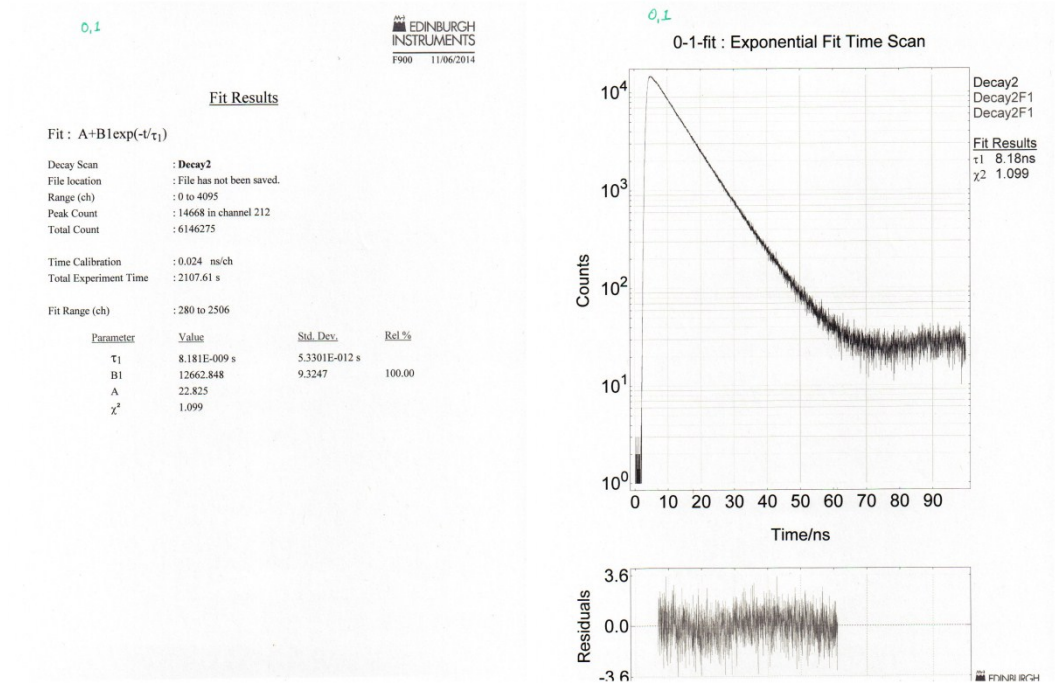
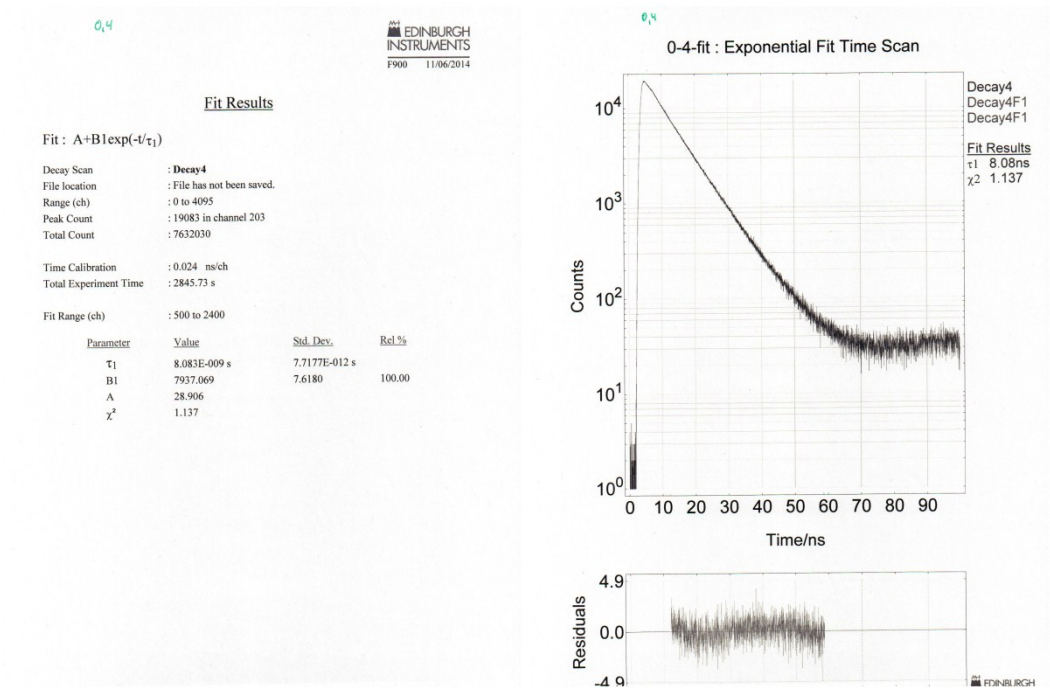


Fig. ESI22 Fit results of [MV^{+2}]/[3HF@$(OA)_2$] in a molar ratio of 0.1 (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).



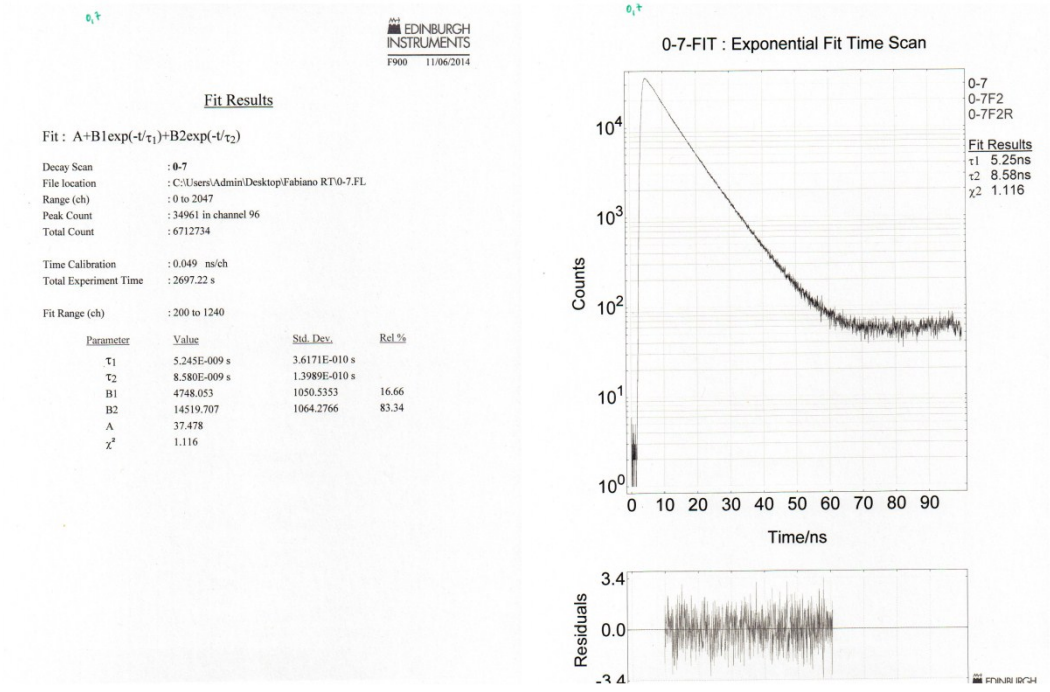
Fit Results

Fit : A+B1exp(-t/τ_1)

Decay Scan	: **Decay4**
File location	: File has not been saved.
Range (ch)	: 0 to 4095
Peak Count	: 19083 in channel 203
Total Count	: 7632030
Time Calibration	: 0.024 ns/ch
Total Experiment Time	: 2845.73 s
Fit Range (ch)	: 500 to 2400

Parameter	Value	Std. Dev.	Rel.%
τ_1	8.083E-009 s	7.7177E-012 s	
B1	7937.069	7.6180	100.00
A	28.906		
χ^2	1.137		

Fig. ESI23 Fit results of [MV^{+2}]/[3HF@$(OA)_2$] in a molar ratio of 0.4 (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).



Fit Results

Fit : A+B1exp(-t/τ_1)+B2exp(-t/τ_2)

Decay Scan	: **0-7**
File location	: C:\Users\Admin\Desktop\Fabiano RT\0-7.FL
Range (ch)	: 0 to 2047
Peak Count	: 34961 in channel 96
Total Count	: 6712734
Time Calibration	: 0.049 ns/ch
Total Experiment Time	: 2697.22 s
Fit Range (ch)	: 200 to 1240

Parameter	Value	Std. Dev.	Rel.%
τ_1	5.245E-009 s	3.6171E-010 s	
τ_2	8.580E-009 s	1.3989E-010 s	
B1	4748.053	1050.5353	16.66
B2	14519.707	1064.2766	83.34
A	37.478		
χ^2	1.116		

Fig. ESI24 Fit results of [MV^{+2}]/[3HF@$(OA)_2$] in a molar ratio of 0.7 (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

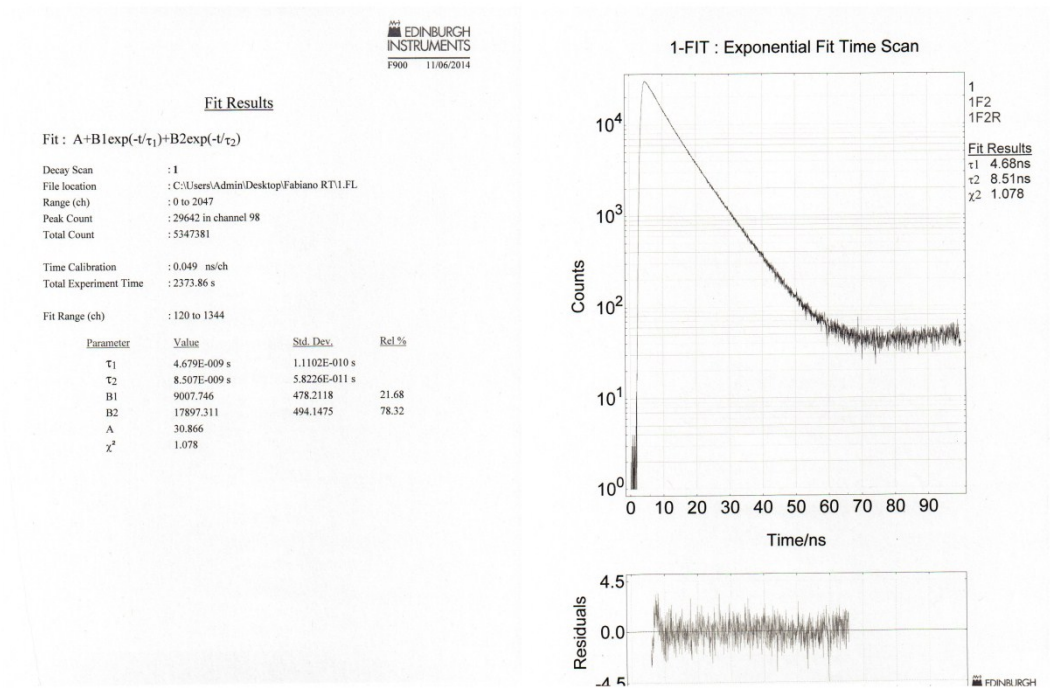


Fig. ESI25 Fit results of $[MV^{+2}]/[3HF@(OA)_2]$ in a molar ratio of 1.0 (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

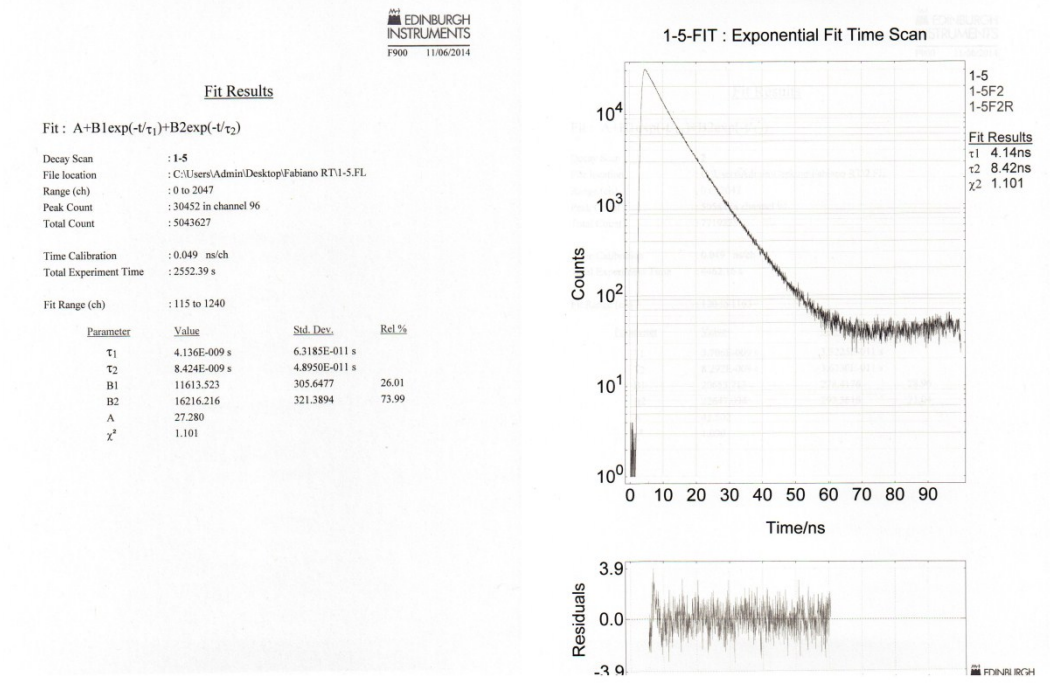


Fig. ESI26 Fit results of $[MV^{+2}]/[3HF@(OA)_2]$ in a molar ratio of 1.5 (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

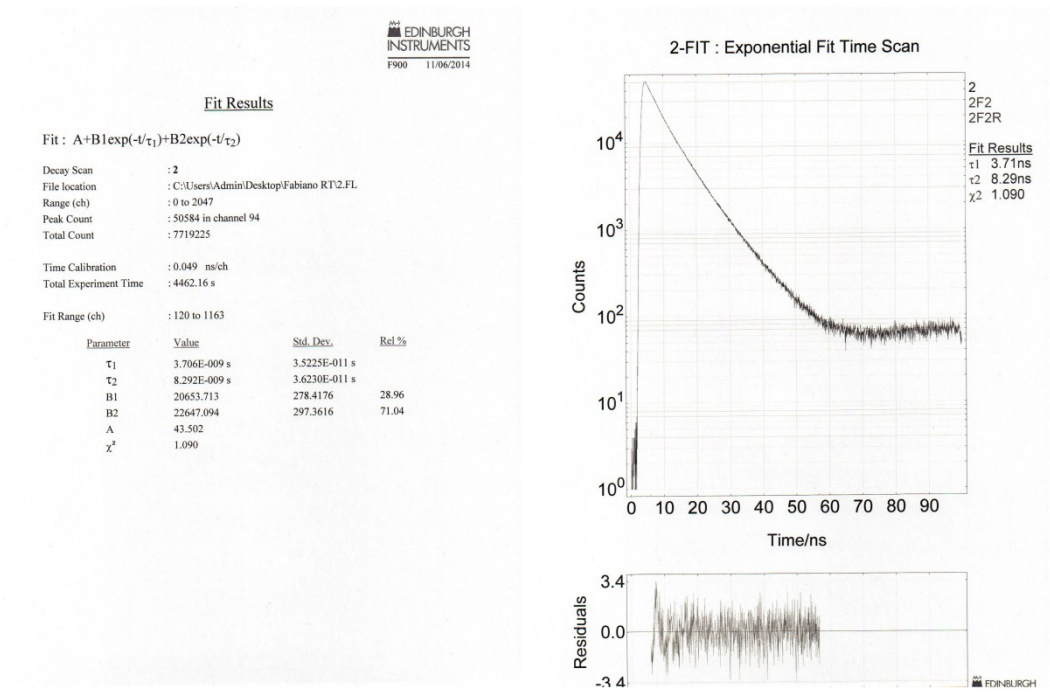


Fig. ESI27 Fit results of $[MV^{+2}]/[3HF@(OA)_2]$ in a molar ratio of 2.0 (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

Titration data of [MP$^+$]/[3HF@(OA)$_2$]

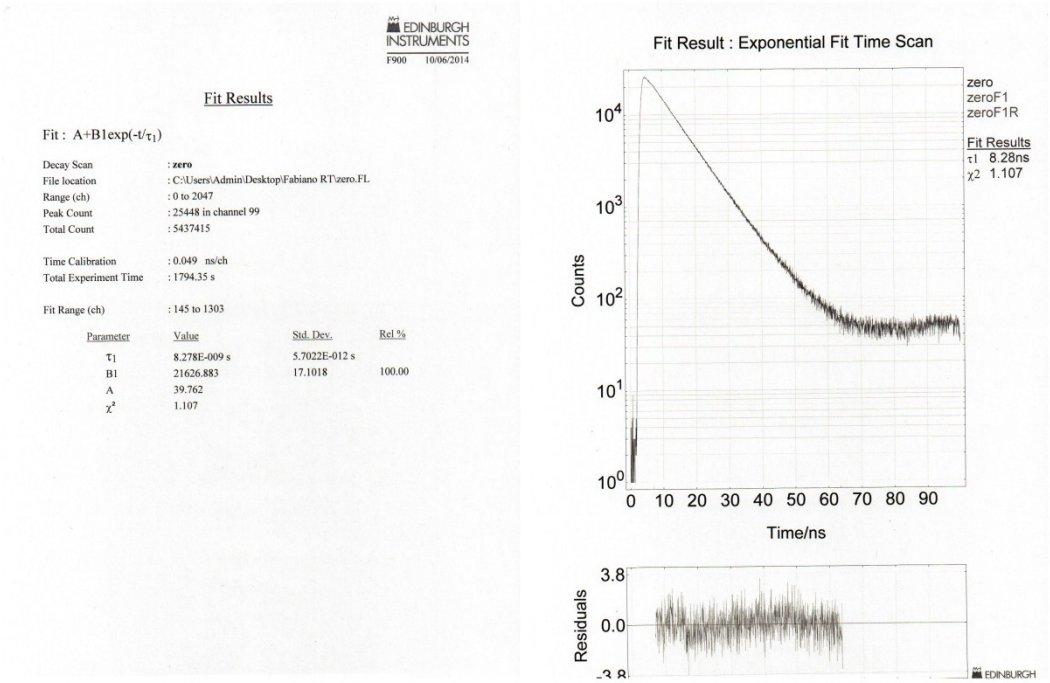


Fig. ESI28 Fit results of 3HF@(OA)$_2$ (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

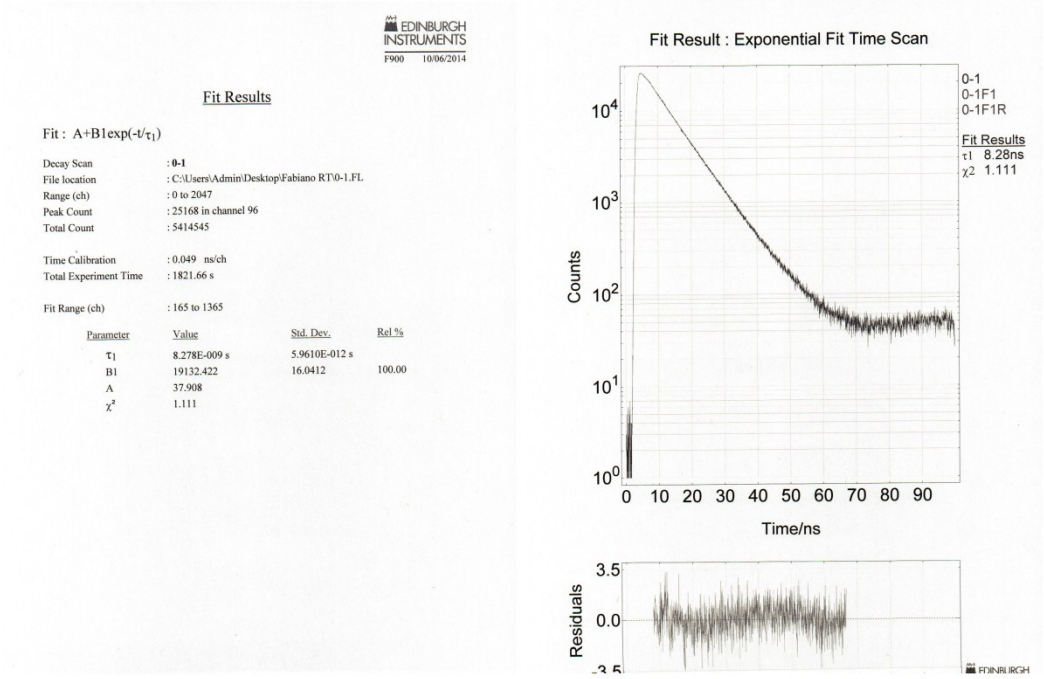


Fig. ESI29 Fit results of [MP$^+$]/[3HF@(OA)$_2$] in a molar ratio of 0.1 (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

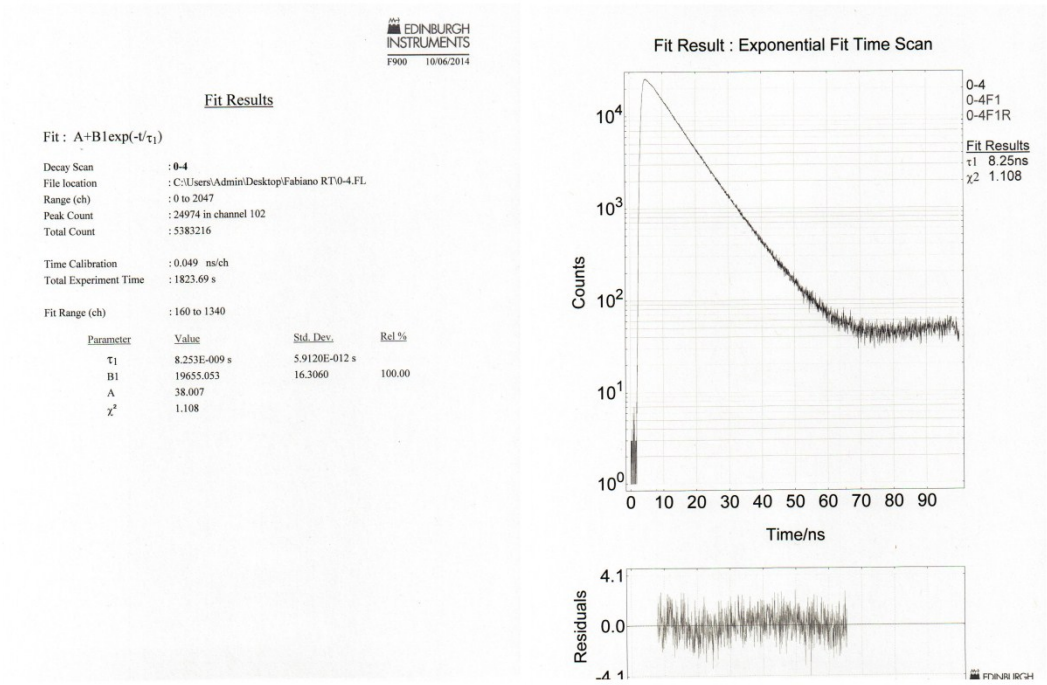


Fig. ESI30 Fit results of [MP$^+$]/[3HF@(OA)$_2$] in a molar ratio of 0.4 (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

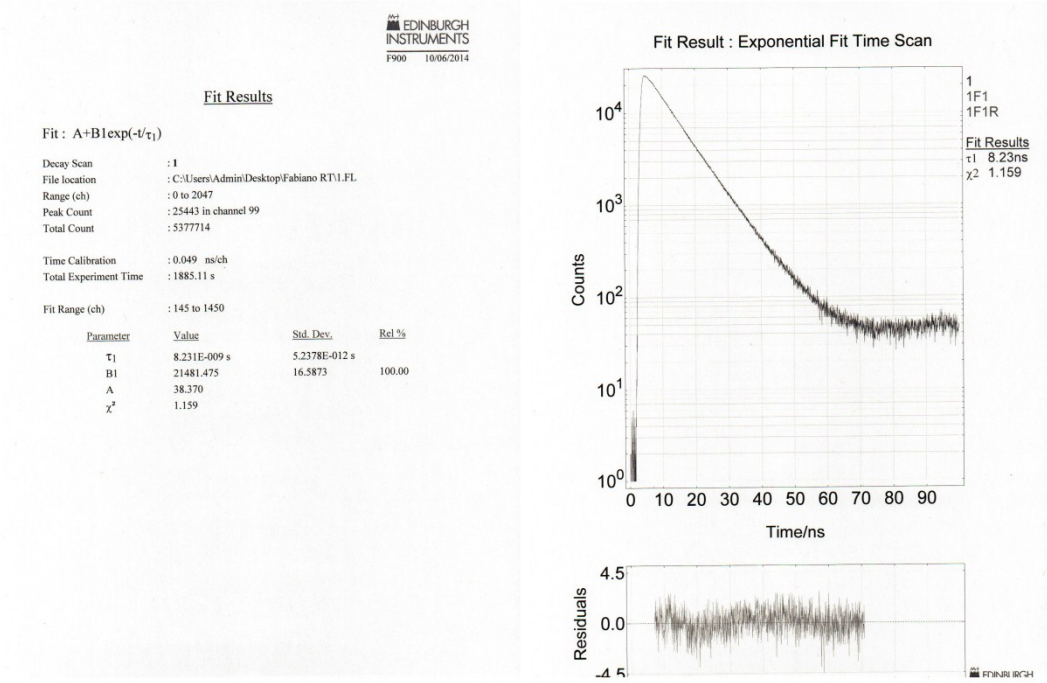


Fig. ESI31 Fit results of [MP$^+$]/[3HF@(OA)$_2$] in a molar ratio of 0.7 (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

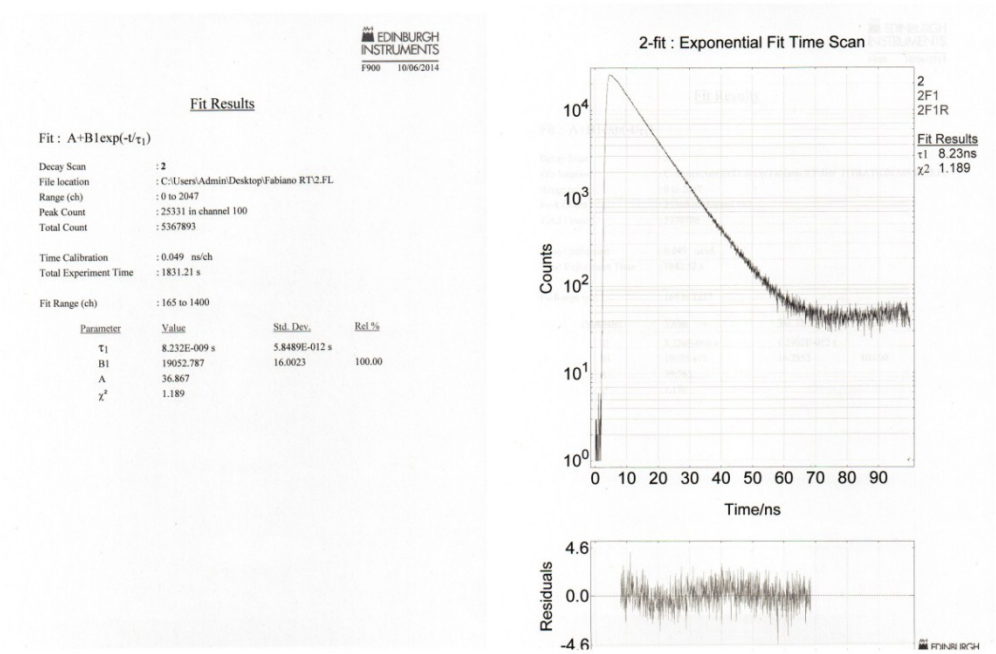


Fig. ESI32 Fit results of [MP$^+$]/[3HF@(OA)$_2$] in a molar ratio of 1.0 (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

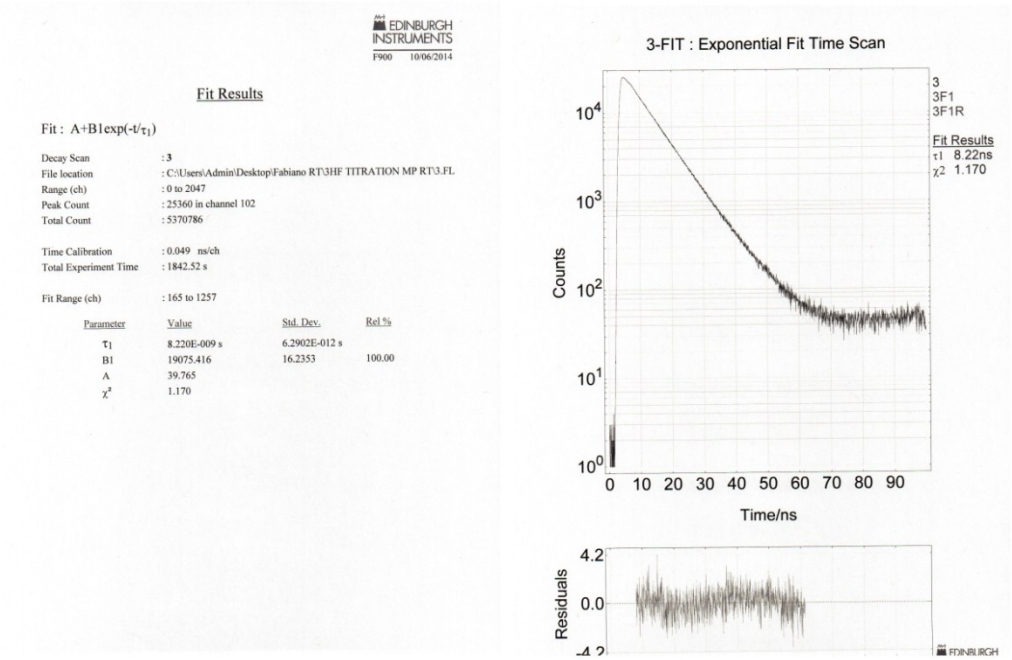


Fig. ESI33 Fit results of [MP$^+$]/[3HF@(OA)$_2$] in a molar ratio of 2.0 (left). Fluorescence decay curves and the residuals for single or double exponential function fits respectively for the same decay data points (right).

PET calculation

Table ESI6. Gibbs free energy for the photoinduced electron transfer process.[a]

Doador	Aceptor	$E_{D/D+}$	$E_{A/A-}$	λ (nm)	ΔE_{00} (KJ/mol)	ΔG (KJ/mol)	ΔG (Kcal/mol)
3HF@$(OA)_2$	MV^{+2}	0.91	-0.69	360	332.3	-177.90	-42.52
	MP^{+}		-1.30			-119.04	-28.45
HBO@$(OA)_2$	MV^{+2}	1.1	-0.69	330	362.5	-189.77	-45.35
	MP^{+}		-1.30			-130.90	-31.29

[a] $\Delta G = 96.50 (E_{D/D+} - E_{A/A-}) - \Delta E_{00}$