Supporting Information

Dual Phosphorescence from the organic and inorganic moieties of 1D Hybrid Perovskites of the $Pb_{n'}Br_{4n'+2}$ Series (n' = 2, 3, 4, 5)

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Table S1- Summary of crystallographic data and structure refinements of $(C_6H_{16}N_2O_2)_3Pb_2Br_{10} \cdot 3H_2O$ (1)

Empirical formula	C18 H48 Br10 N6 O9 Pb2
Formula weight	1712.02
Temperature	150(10) K
Wavelength	1.54184 A
Crystal system, space group	Monoclinic, P 21
Unit cell dimensions	a = 8.1393(3) A alpha = 90 deg.
	b = 25.2015(9) A beta = 91.088(3) deg.
	c = 10.9881(5) A gamma = 90 deg.
Volume	2253.50(15) A^3
Z, Calculated density	4, 2.514 Mg/m^3
Absorption coefficient	25.119 mm^-1
F(000)	1568
Theta range for data collection	3.508 to 72.633 deg.
Limiting indices	-10<=h<=8, -30<=k<=30, -11<=l<=13
Reflections collected / unique	9248 / 6698 [R(int) = 0.0636]
Completeness to theta = 69.000	99.5 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6698 / 1 / 404
Goodness-of-fit on F^2	1.013
Final R indices [I>2sigma(I)]	R1 = 0.0576, wR2 = 0.1458
R indices (all data)	R1 = 0.0684, wR2 = 0.1516
Absolute structure parameter	-0.023(15)
Extinction coefficient	0.00007(5)
Largest diff. peak and hole	2.190 and -2.268 e.A^-3

Table S2- Summary of crystallographic data and structure refinements of $(C_5H_{15}N_2O_2)_4Pb_3Br_{14}.2H_2O$ (2)

Empirical formula	C20 H64 Br14 N8 O10 Pb3
Formula weight	2317.10
Temperature	150(10) K
Wavelength	1.5418 A
Crystal system, space group	Triclinic, P 1
Unit cell dimensions	a = 8.274(5) A alpha = 71.769(5) deg.
	b = 11.580(5) A beta = 77.947(5) deg.
	c = 15.717(5) A gamma = 72.105(5) deg.
Volume	1350.5(11) A^3
Z, Calculated density	1, 2.849 Mg/m^3
Absorption coefficient	30.423 mm^-1
F(000)	1056
Theta range for data collection	2.983 to 72.610 deg.
Limiting indices	-10<=h<=10, -14<=k<=13, -19<=l<=19
Reflections collected / unique	22457 / 9754 [R(int) = 0.0482]
Completeness to theta = 70.000	99.4 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9754 / 9 / 494
Goodness-of-fit on F^2	1.015
Final R indices [I>2sigma(I)]	R1 = 0.0306, wR2 = 0.0738
R indices (all data)	R1 = 0.0325, wR2 = 0.0745
Absolute structure parameter	0.011(7)
Extinction coefficient	0.00015(2)
Largest diff. peak and hole	1.310 and -1.415 e.A^-3

Table S3- Summary of crystallographic data and structure refinements of $(C_6H_{16}N_2O_2)_6Pb_4Br_{18} \cdot 2Br.2H_2O$ (3)

```
Empirical formula                  C36 H100 Br20 N12 O14 Pb4
Formula weight                     3352.24
Temperature                        150.0(1) K
Wavelength                         1.54184 A
Crystal system, space group        Monoclinic,  P 21
Unit cell dimensions        a = 12.3316(4) A    alpha = 90 deg.
                            b = 8.0863(2) A      beta = 101.621(3)
deg.
                            c = 23.0098(7) A    gamma = 90 deg.
Volume                             2247.44(12) A^3
Z, Calculated density              1,  2.477 Mg/m^3
Absorption coefficient             25.132 mm^-1
F(000)                             1540
Crystal size                       0.243 x 0.097 x 0.042 mm
Theta range for data collection    3.788 to 72.403 deg.
Limiting  indices                     -13<=h<=14,  -6<=k<=9,  -
26<=l<=28
Reflections collected / unique     9202 / 5750 [R(int) = 0.0483]
Completeness to theta = 70.000     99.3 %
Absorption correction              Semi-empirical from equivalents
Max. and min. transmission         1.00000 and 0.58612
Refinement method                     Full-matrix least-squares on
F^2
Data / restraints / parameters     5750 / 33 / 418
Goodness-of-fit on F^2             1.004
Final R indices [I>2sigma(I)]     R1 = 0.0599, wR2 = 0.1649 [5471
Fo]
R indices (all data)              R1 = 0.0621, wR2 = 0.1686
Absolute structure parameter      -0.027(14)
Largest diff. peak and hole        3.787 and -3.426 e.A^-3
```

Table S4- Summary of crystallographic data and structure refinements of $(C_6H_{16}N_2O_2)_6Pb_5Br_{22} \cdot 4H_2O$ (4)

```
Empirical formula                      C36 H104 Br22 N12 O16 Pb5

   Formula weight                      3755.28
   Temperature                         150.0(1) K
   Wavelength                          1.54184 A
   Crystal system, space group         Monoclinic,  P 21/c
   Unit cell dimensions          a = 26.7956(13) A   alpha = 90 deg.
                                 b =  8.1729(3) A     beta = 112.775(6)
deg.
                                 c = 22.9805(11) A   gamma = 90 deg.
   Volume                              4640.3(4) A^3
   Z, Calculated density               2,  2.688 Mg/m^3
   Absorption coefficient              28.828 mm^-1
   F(000)                              3424
   Crystal size                        0.31 x 0.084 x 0.062 mm
   Theta range for data collection     3.578 to 72.669 deg.
   Limiting indices                        -32<=h<=28,  -6<=k<=9,  -
28<=l<=28
   Reflections collected / unique      18103 / 8948 [R(int) = 0.0635]
   Completeness to theta = 71.500      98.4 %
   Absorption correction               Semi-empirical from equivalents
   Max. and min. transmission          1.00000 and 0.58122
   Refinement method                      Full-matrix least-squares on
F^2
   Data / restraints / parameters      8948 / 36 / 419
   Goodness-of-fit on F^2              0.988
   Final R indices [I>2sigma(I)]      R1 = 0.0499, wR2 = 0.1100   [6517
fo]
   R indices (all data)               R1 = 0.0775, wR2 = 0.1248
   Largest diff. peak and hole        2.326 and -2.762 e.A^-3
```

Table S5 Emission properties of the four compounds as crystallized powders, compound 2 cast film and organic salts

	Abs λ_{max} (nm)	PL Excitation λ_{max} (nm)	PL Emission λ_{max} (nm)	QY (%)	PL τ_{av} (ns) exc300	Ph Excitation λ_{max} (nm)	Ph Emission λ_{max} (nm)	Phos τ_{av} (ms)
1		290,320, 356 380, 402[sh]	635 398,418,440	0.10	< 0.3 (390) 1.06 (418)	380 420 440 480	570 (exc380) 590 (exc408) 630 (exc420) 710 (exc480)	4.66 4.43
2 cryst RT		295,335,366,	390, 545	13.46	16.5 (390) 97.8 (560)	394 421	557 (exc393) 595 (exc422) 570 (exc365)	10.93 5.99 2.80
2 cryst LT		290,340,357,398,	570		5.25 (410) 76.63 (570)	280, 395	400 (exc300) 600 (exc300) 590 (exc390)	19.09 11.84
2 film RT	260,316, 388	287,402 284,371	404, 560		3.13	362,406	610 (ex340,400) 595 (exc300)	1.26-2.46
2 film LT		277,316,388 277,348,376,401	402, 620		3.82 (403) 48.64 (620)	287,395	403 620	5.47 4.87
3		275, 345, 375	390-420 , 575	27.74	20.4 (390) 36.0 (575)	395, 386, 422[sh]	520(exc395) 600 (exc422)	5.34 3.35
4		280,380	410, 560	8.50	12.3 (400) 3449 (555)	395, 417	560	4.27
H₂Orn²⁺		275, 410-420	490-515	<0.1	3.9 (480em)	295, 360	530-570	43
H₂Lys²⁺		280, 365	390-415 575	<0.1	19.7-24.5 3.23 (575)	293, 360	515 520 (Br salt)	69 6.2 (Br salt)

$$\tau_{av} = \sum_i \frac{A_i \tau_i^2}{A_i \tau_i}$$

$$<t> = \sum_i \frac{A_i \tau_i}{A_i}$$

Figure S1- Powder X-ray diffraction of $(C_6H_{16}N_2O_2)_3Pb_2Br_{10} \cdot 3H_2O$ (1) : experimental (crystallized powder) and theoretical
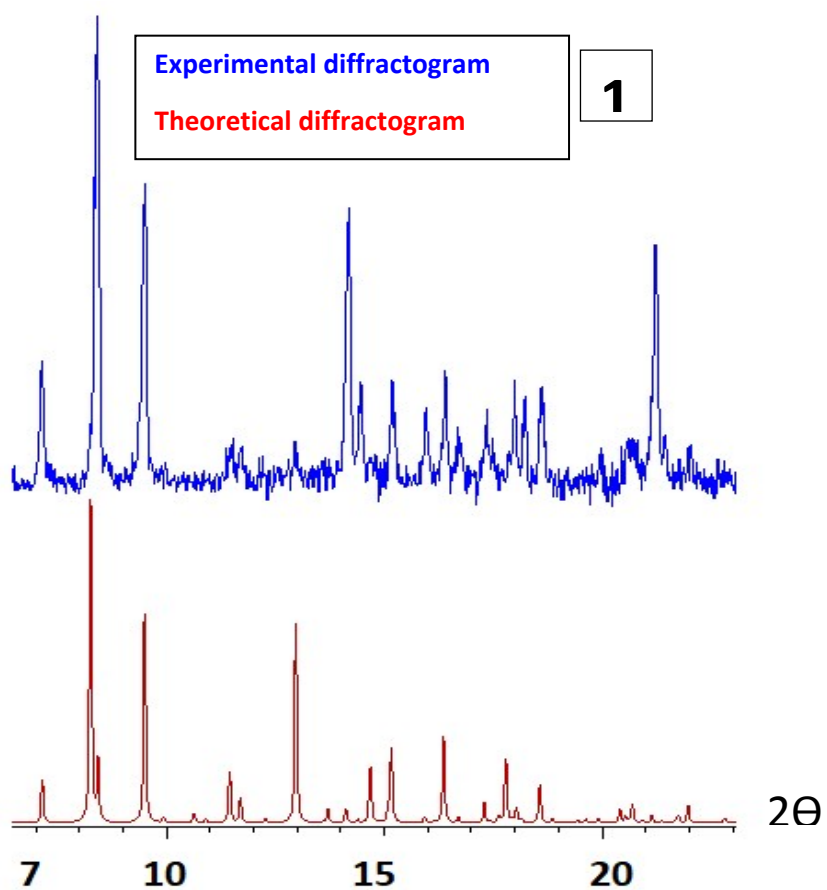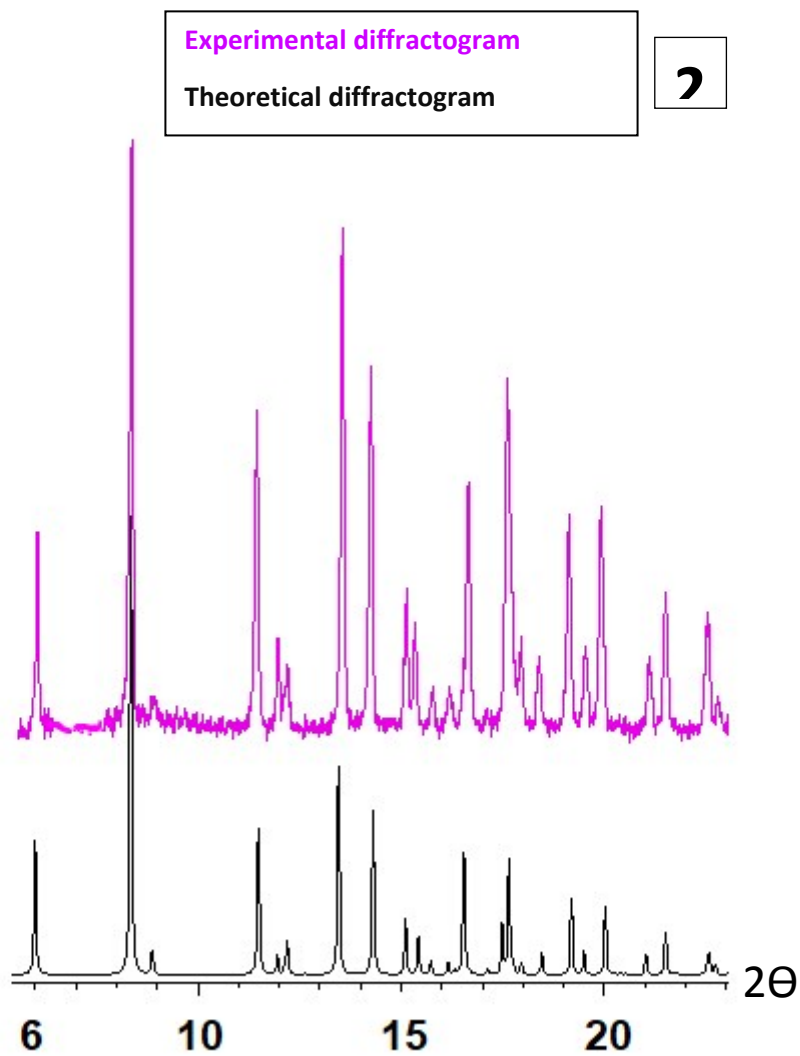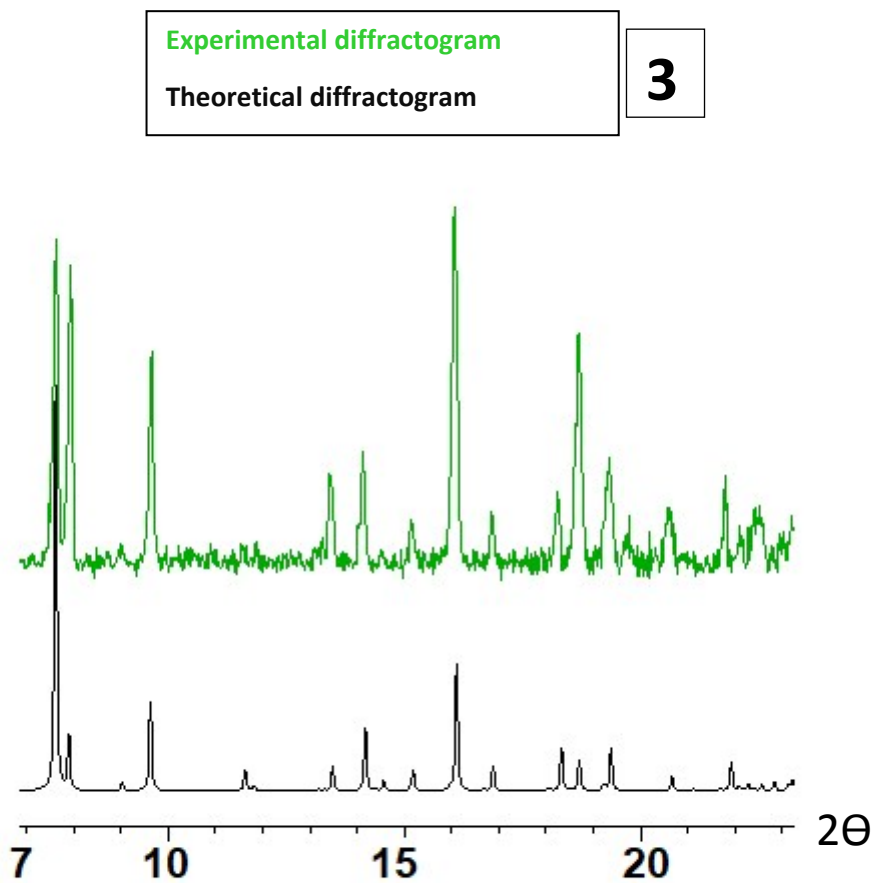
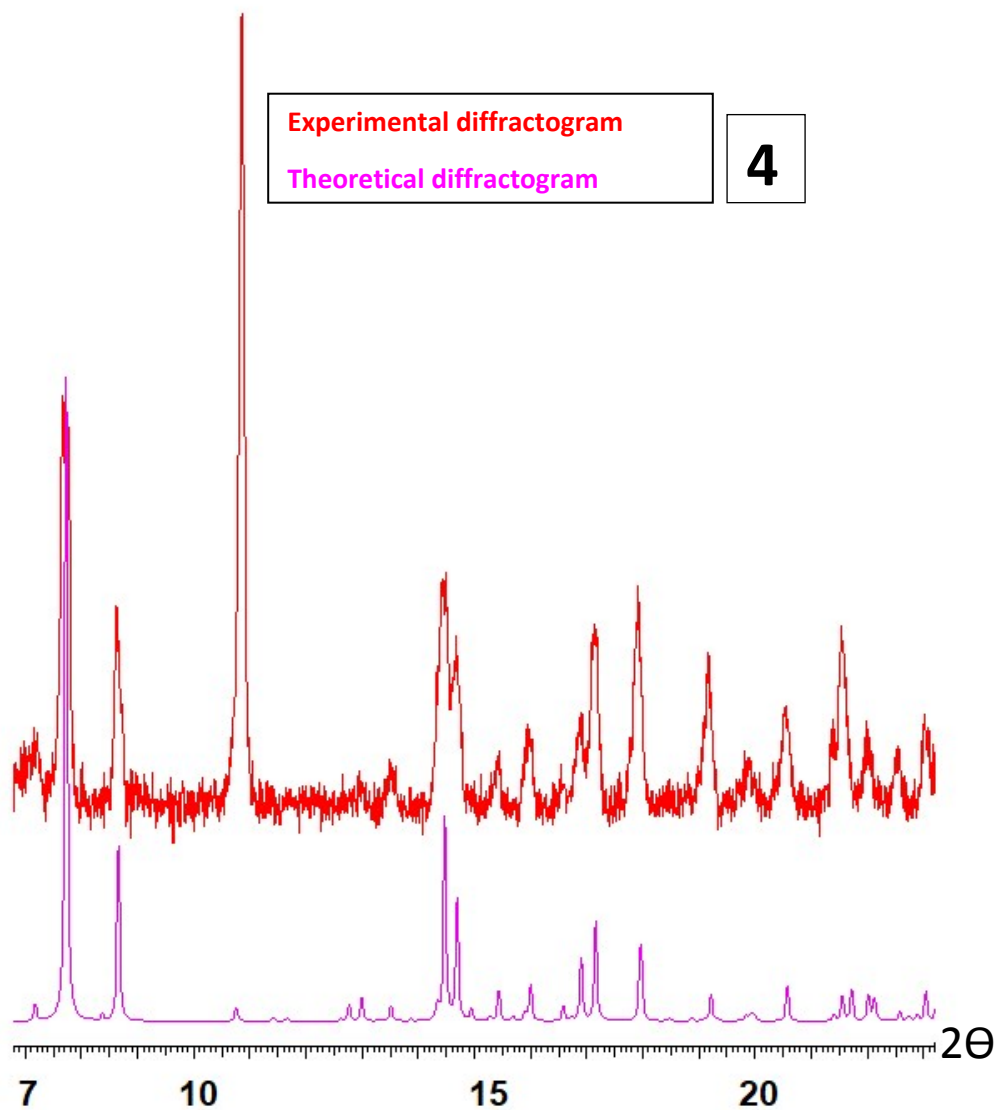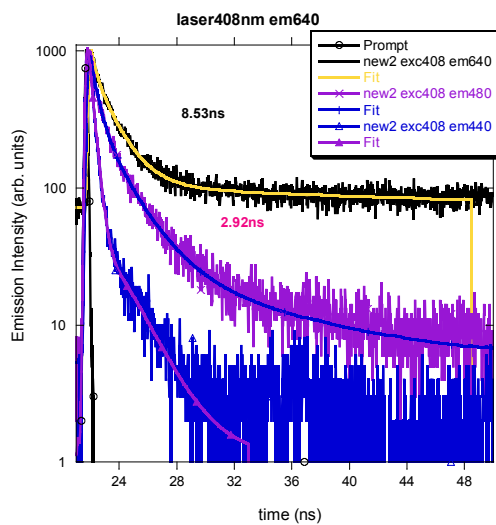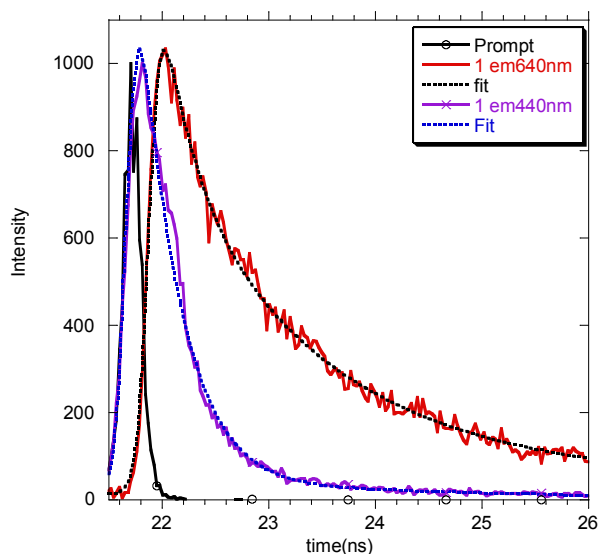Experimental diffractogram

Theoretical diffractogram

1

2θ

7   10   15   20

Figure S2- Powder X-ray diffraction of $(C_5H_{15}N_2O_2)_4Pb_3Br_{14}.2H_2O$ (2) : experimental (crystallized powder) and theoretical

Figure S3- Powder X-ray diffraction of $(C_6H_{16}N_2O_2)_6Pb_4Br_{18}. 2Br.2H_2O$ (3) : experimental (crystallized powder) and theoretical

Experimental diffractogram

Theoretical diffractogram

3

2Θ

Figure S4- Powder X-ray diffraction of $(C_6H_{16}N_2O_2)_6Pb_5Br_{22}$ .4H$_2$O (4) : experimental (crystallized powder) and theoretical

Experimental diffractogram

Theoretical diffractogram

4

2θ

em440nm
T1 = 17.63099 ch¬
 4.78388E-10 sec¬
 S.Dev = 8.672142E-11 sec¬
T2 = 70.3792 ch¬
 1.909624E-09 sec¬
 S.Dev = 1.197626E-10 sec¬
T3 = 17.43742 ch¬
 4.731357E-10 sec¬
 S.Dev = 2.549723E-11 sec¬

A = 1.103473¬
 S.Dev = 8.204465E-02¬

B1 = -5.350416¬
 [-2649.92 Rel.Ampl]¬
 S.Dev = 0.1693577¬
B2 = 0.0129075¬
 [25.52 Rel.Ampl]¬
 S.Dev = 3.460021E-04¬
B3 = 5.561865¬
 [2724.40 Rel.Ampl]¬
 S.Dev = 0.1706665¬
¬

CHISQ = 1.173708¬

480nm
T1 = 72.72403 ch¬
 1.973247E-09 sec¬
 S.Dev = 9.84667E-11 sec¬
T2 = 333.0858 ch¬
 9.037736E-09 sec¬
 S.Dev = 5.142823E-10 sec¬
T3 = 18.89258 ch¬
 5.126192E-10 sec¬
 S.Dev = 1.701062E-11 sec¬

A = 5.302193¬
 S.Dev = 0.0775927¬

B1 = 4.865745E-02¬
 [49.58 Rel.Ampl]¬
 S.Dev = 6.579388E-04¬
B2 = 4.242538E-03¬
 [19.80 Rel.Ampl]¬
 S.Dev = 1.068943E-04¬
B3 = 0.1156497¬
 [30.62 Rel.Ampl]¬
 S.Dev = 1.780917E-03¬

CHISQ = 1.25222¬

em640nm
T1 = 54.59367 ch¬
 1.48131E-09 sec¬
 S.Dev = 4.44587E-11 sec¬
T2 = 767.1806 ch¬
 2.081619E-08 sec¬
 S.Dev = 2.018351E-09 sec¬
T3 = 9.842682 ch¬
 2.67065E-10 sec¬
 S.Dev = 3.522658E-11 sec¬

A = 72.19673¬
 S.Dev = 0.6508875¬

B1 = 0.1023323¬
 [56.17 Rel.Ampl]¬
 S.Dev = 9.166764E-04¬
B2 = 4.77952E-03¬
 [36.87 Rel.Ampl]¬
 S.Dev = 1.907356E-04¬
B3 = 7.032902E-02¬
 [6.96 Rel.Ampl]¬
 S.Dev = 0.0028891¬

CHISQ = 1.200694¬

Fig.S5 PL decay of compound **1**, at RT, exc 408nm, emission at 640nm, 440nm and 480nm. 3exp fit: (480nm: $<\tau>$=1.159ns; τ_{av}=2.92ns; 560nm: $<\tau>$=1.52ns; τ_{av}=8.53 ns
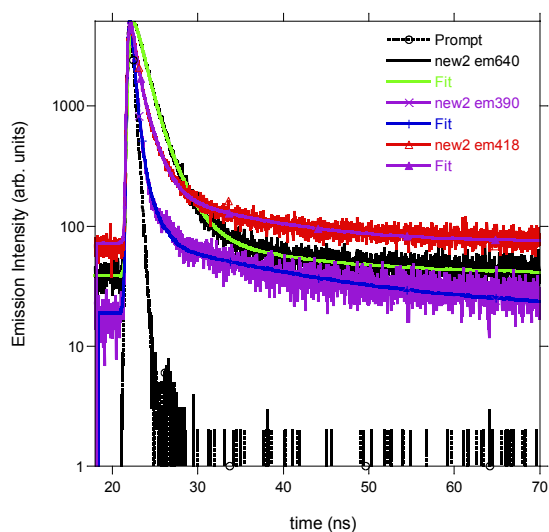
Fig.S6 PL decay of compound **1**, at RT, exc 300 nm, emission at 640, 390 and 418nm, with 3exp fits (418nm: $<\tau>$=0.31ns; τ_{av}=1.06ns; 560nm: $<\tau>$=1.14ns; τ_{av}=2.45 ns).
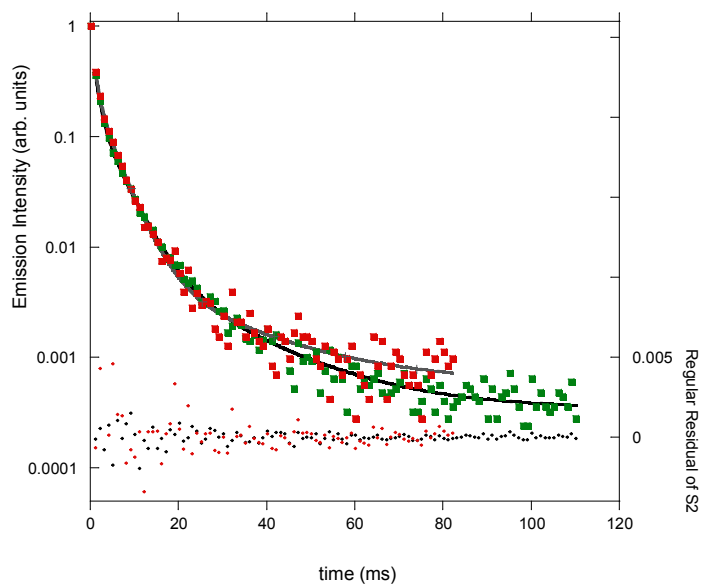

Fig.S7 Ph decay of compound **1**, at RT, exc 380 nm (emission at 600nm, τ_{av}=4.66ms), exc 420 (emission at 640nm τ_{av}=4.43ms).

T1 = 245.7889 ch¬
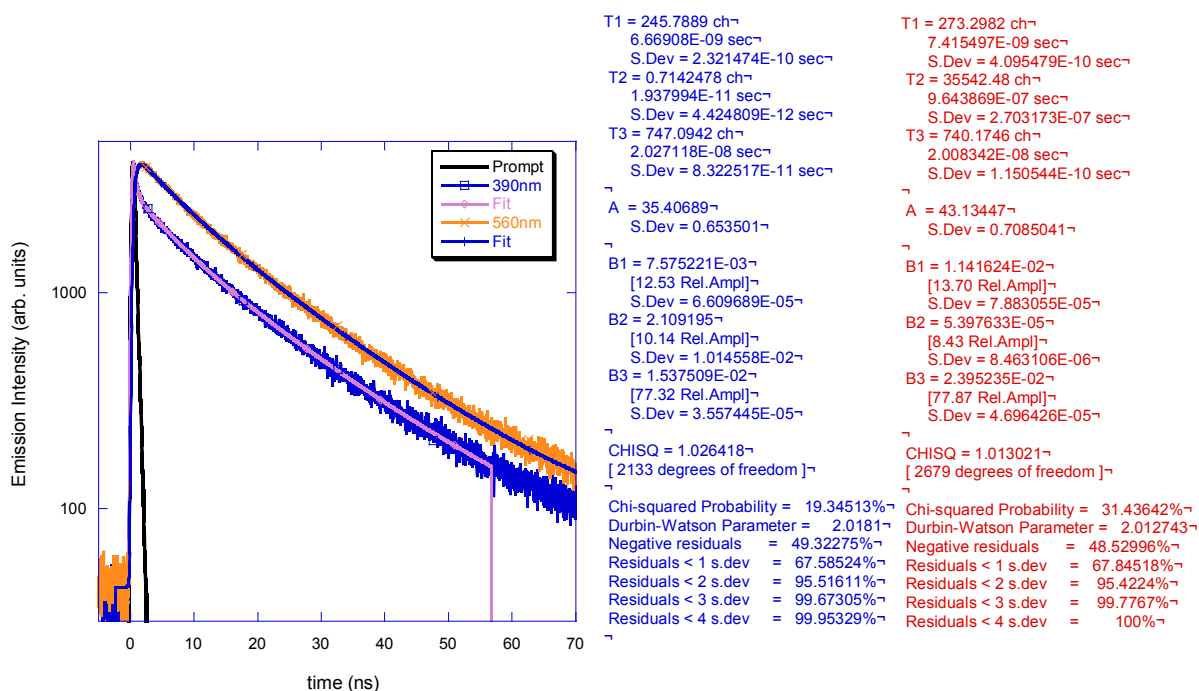 6.66908E-09 sec¬
  S.Dev = 2.321474E-10 sec¬
T2 = 0.7142478 ch¬
  1.937994E-11 sec¬
  S.Dev = 4.424809E-12 sec¬
T3 = 747.0942 ch¬
  2.027118E-08 sec¬
  S.Dev = 8.322517E-11 sec¬
¬
A = 35.40689¬
  S.Dev = 0.653501¬
¬
B1 = 7.575221E-03¬
  [12.53 Rel.Ampl]¬
  S.Dev = 6.609689E-05¬
B2 = 2.109195¬
  [10.14 Rel.Ampl]¬
  S.Dev = 1.014558E-02¬
B3 = 1.537509E-02¬
  [77.32 Rel.Ampl]¬
  S.Dev = 3.557445E-05¬
¬
CHISQ = 1.026418¬
[2133 degrees of freedom]¬

Chi-squared Probability = 19.34513%¬
Durbin-Watson Parameter = 2.0181¬
Negative residuals   = 49.32275%¬
Residuals < 1 s.dev   = 67.58524%¬
Residuals < 2 s.dev   = 95.51611%¬
Residuals < 3 s.dev   = 99.67305%¬
Residuals < 4 s.dev   = 99.95329%¬
¬

T1 = 273.2982 ch¬
  7.415497E-09 sec¬
  S.Dev = 4.095479E-10 sec¬
T2 = 35542.48 ch¬
  9.643869E-07 sec¬
  S.Dev = 2.703173E-07 sec¬
T3 = 740.1746 ch¬
  2.008342E-08 sec¬
  S.Dev = 1.150544E-10 sec¬
¬
A = 43.13447¬
  S.Dev = 0.7085041¬
¬
B1 = 1.141624E-02¬
  [13.70 Rel.Ampl]¬
  S.Dev = 7.883055E-05¬
B2 = 5.397633E-05¬
  [8.43 Rel.Ampl]¬
  S.Dev = 8.463106E-06¬
B3 = 2.395235E-02¬
  [77.87 Rel.Ampl]¬
  S.Dev = 4.696426E-05¬
¬
CHISQ = 1.013021¬
[2679 degrees of freedom]¬

Chi-squared Probability = 31.43642%¬
Durbin-Watson Parameter = 2.012743¬
Negative residuals   = 48.52996%¬
Residuals < 1 s.dev   = 67.84518%¬
Residuals < 2 s.dev   = 95.4224%¬
Residuals < 3 s.dev   = 99.7767%¬
Residuals < 4 s.dev   = 100%¬

Fig.S8 PL decay of compound **2**, at RT, exc 300 nm, emission at 560, and 390 nm, with 3exp fits (390nm: $<\tau>$=0.19ns; τ_{av}=16.51ns; 560nm: $<\tau>$=17.44ns; τ_{av}=97.82 ns
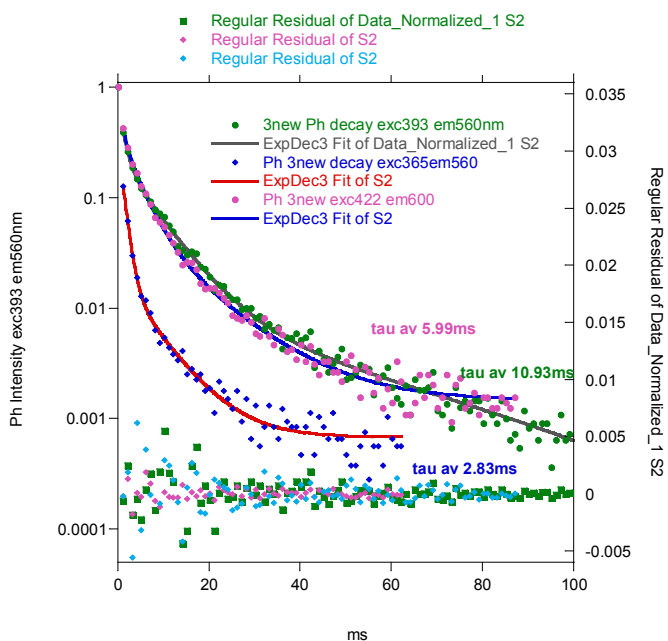

Fig.S9 Ph decay of compound **2** at RT, exc 393 em 560nm; exc 422, em 600nm; exc 365, em560nm. 3exp fit: Emission at 560nm: exc 393, $<\tau>$=3.57ms, τ_{av} = 10.93ms; exc 365nm, $<\tau>$=1.48ms; ns τ_{av} = 2.83 ms ; em 600: $<\tau>$=2.81ms, τ_{av} = 5.99ms

300nm decay4new

T1 = 40.75559 ch¬
    1.105836E-09 sec¬
    S.Dev = 4.070668E-11 sec¬
T2 = 1462.522 ch¬
    3.968314E-08 sec¬
    S.Dev = 1.353118E-10 sec¬
T3 = 0.3159901 ch¬
    8.573873E-12 sec¬
    S.Dev = 1.975761E-12 sec¬
¬
A = 148.6884¬
    S.Dev = 1.155483¬
¬
B1 = 3.836054E-03¬
    [1.16 Rel.Ampl]¬
    S.Dev = 6.666117E-05¬
B2 = 4.735677E-03¬
    [51.44 Rel.Ampl]¬
    S.Dev = 8.497526E-06¬
B3 = 20.20067¬
    [47.40 Rel.Ampl]¬
    S.Dev = 5.328399E-02¬
¬
CHISQ = 1.017789¬
[2284 degrees of freedom]¬

T1 = 977.6738 ch¬
    2.652758E-08 sec¬
    S.Dev = 2.725376E-09 sec¬
T2 = 140.6066 ch¬
    3.81513E-09 sec¬
    S.Dev = 3.276294E-10 sec¬
T3 = 1024.502 ch¬
    2.779818E-08 sec¬
    S.Dev = 2.556337E-10 sec¬
¬
A = 793.2278¬
    S.Dev = 2.485044¬
¬
B1 = -0.2928481¬
    [-664.22 Rel.Ampl]¬
    S.Dev = 9.172593E-04¬
B2 = 0.0030182¬
    [0.98 Rel.Ampl]¬
    S.Dev = 6.800162E-05¬
B3 = 0.3211224¬
    [763.23 Rel.Ampl]¬
    S.Dev = 8.938007E-04¬
¬
CHISQ = 1.112282¬
[2394 degrees of freedom]¬
¬

Fig.S10 PL time decay of compound **3**, exc300nm em390nm and 575nm. Emission at 390nm: <τ>=0.02ns, τ_{av} = 20.43 ns; Emission at 575nm: ns τ_{av} = 36.00 ns ;

decay exc395 em500
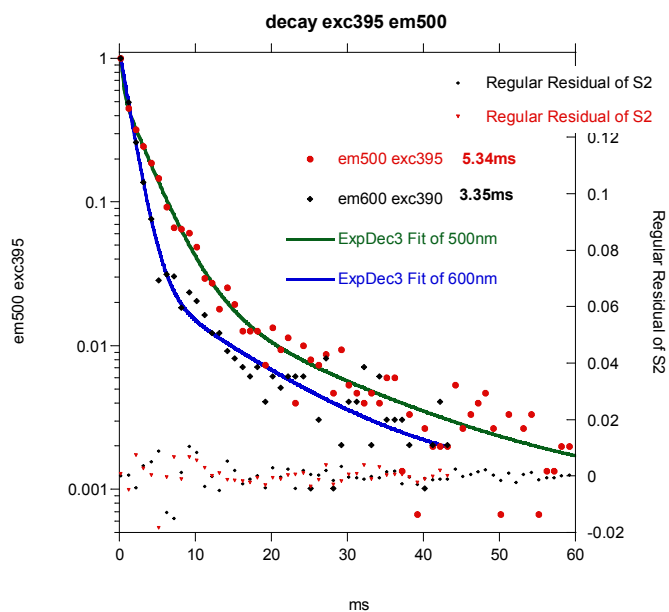
Fig.S11 Ph time decay of compound **3**, at RT, exc395nm em500nm; exc390 em600.
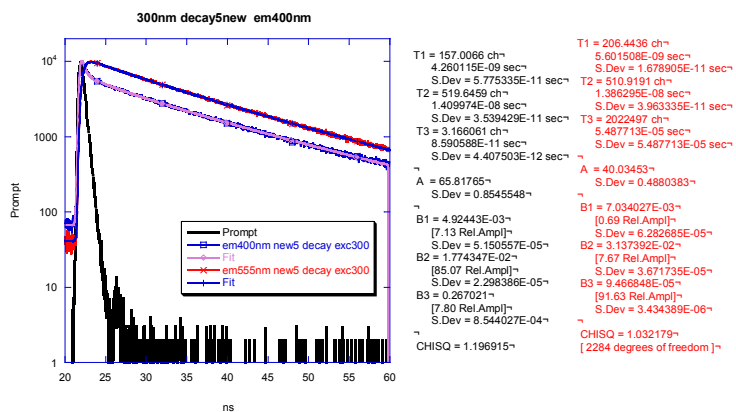
Fig.S12 PL time decay of compound **4**, exc300nm emission at 400nm and 555nm. Emission at 400nm: <τ>=1ns, τ_{av} = 12.30 ns; Emission at 555nm: ns <τ>=21.35ns τ_{av} = 3449 ns ;
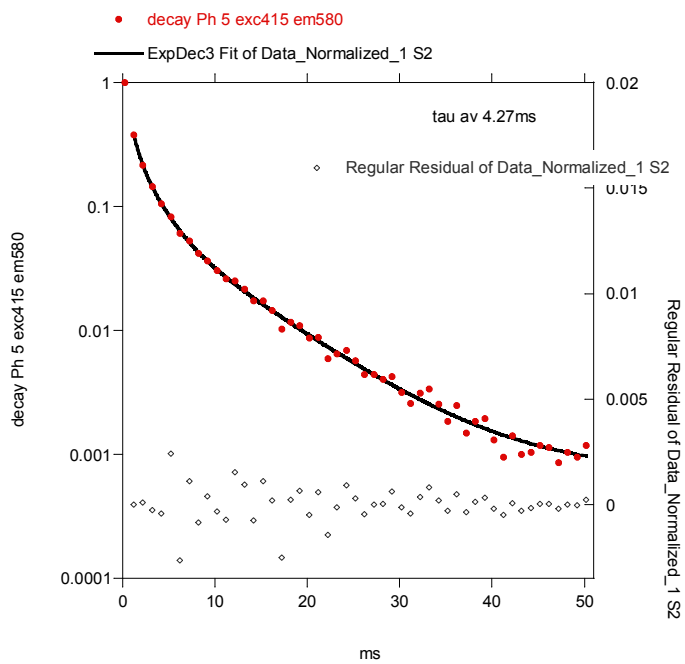
Fig.S13 Ph time decay of compound **4**, exc415nm, em580nm

PL RT exc310 F325
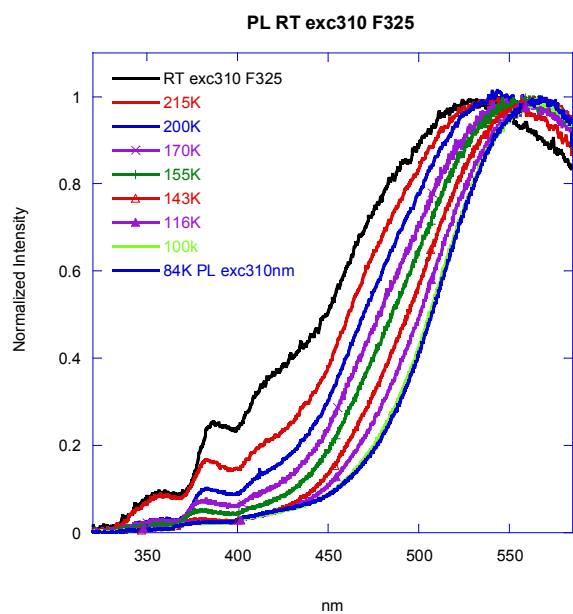
Fig.S14 Temperature evolution of the emission of compound **2** crystal powders. Normalized spectra.

decay 84k laser408
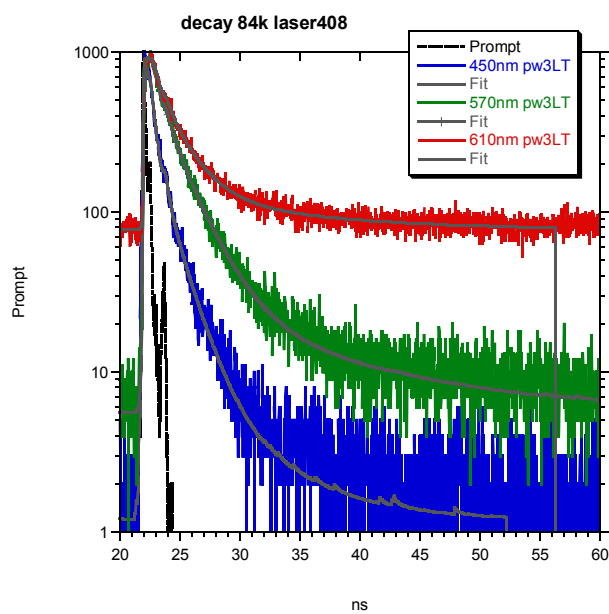
Fig.S15 PL time decay of compound **2** at LT, exc 408nm. 3exp fit: Emission at 450nm: $\langle\tau\rangle$=0.55ns, τ_{av} = 1.13 ns; 610nm: $\langle\tau\rangle$=1.68ns; ns τ_{av} = 4.0 ns ;
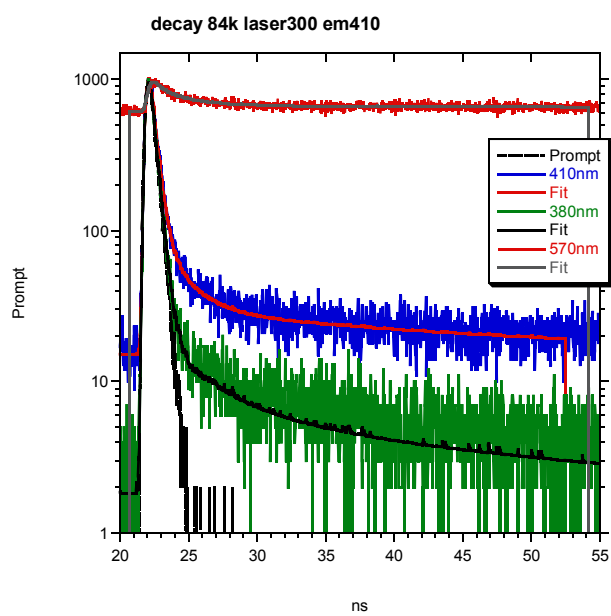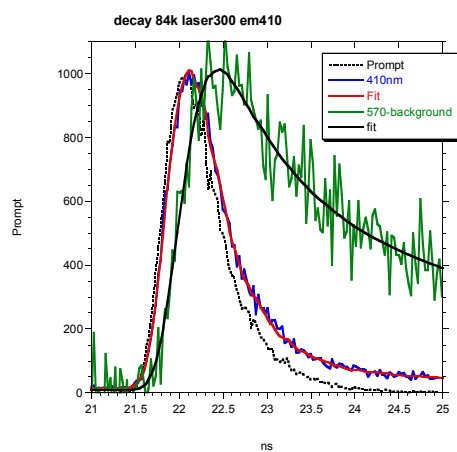
Fig.S16 PL time decay of compound **2** at LT, exc 300nm. Emission at 410nm: $\langle\tau\rangle$=0.07ns, τ_{av} = 5.25 ns; 570nm: $\langle\tau\rangle$=5.49ns; ns τ_{av} = 76.63 ns ;
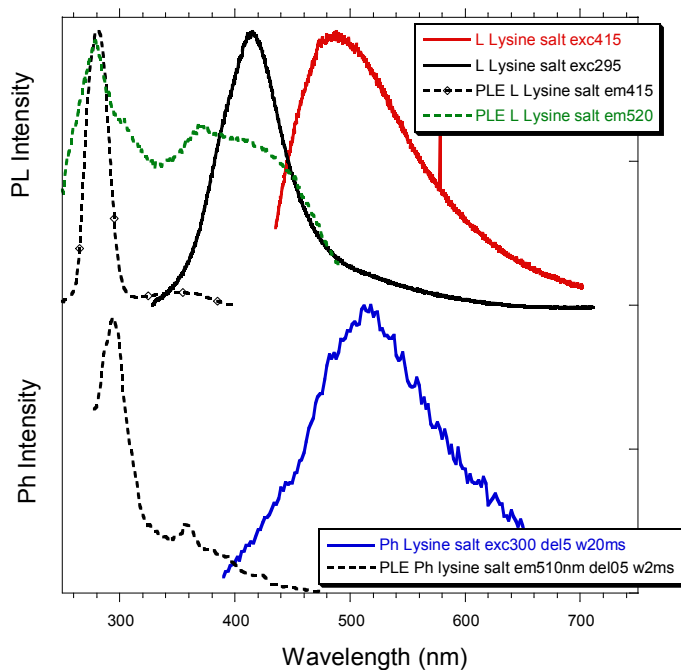
Fig.S17 PL and Ph properties of Lysine Cl salt at RT
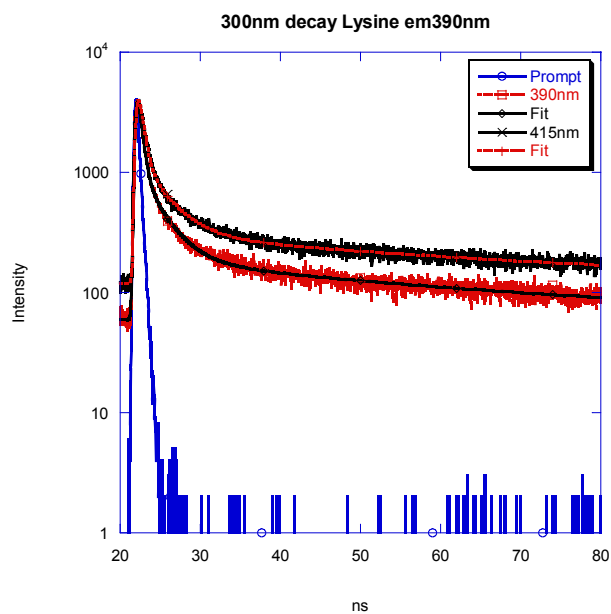
Fig.S18 PL time decay of Lysine Cl salt, exc300nm, emission at 390nm $<\tau>$=1.04ns, τ_{av} = 19.69ns; . Emission at 415nm: $<\tau>$=1.65ns ns; τ_{av} = 24.646ns
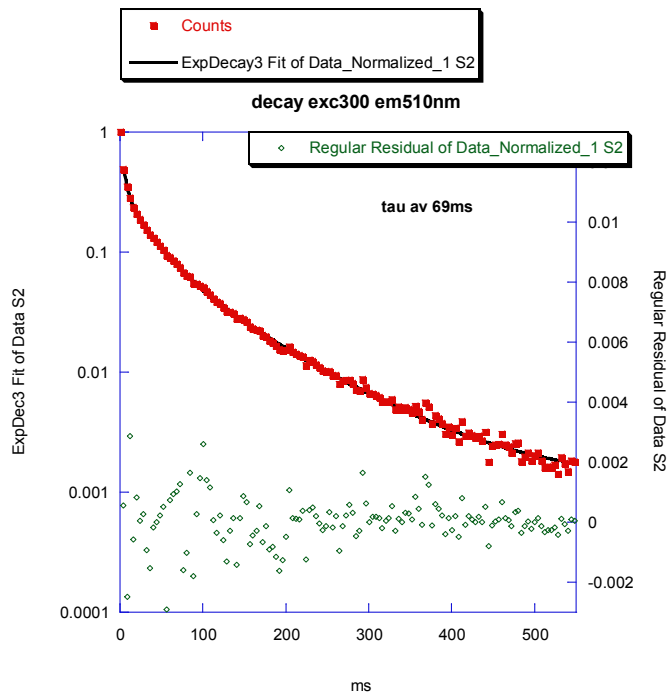
Fig.S19 Ph time decay of Lysine Cl salt, exc300nm, emission at 510nm
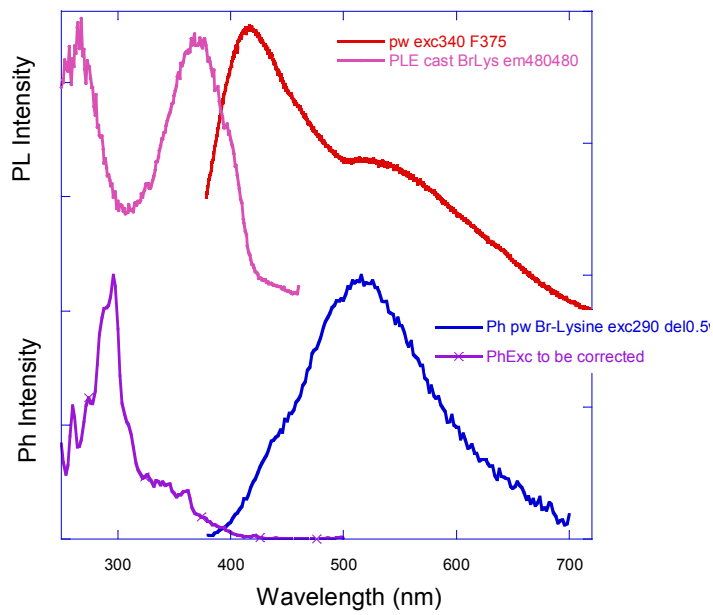
Fig.S20 PL and Ph properties of Lysine Br salt, at RT
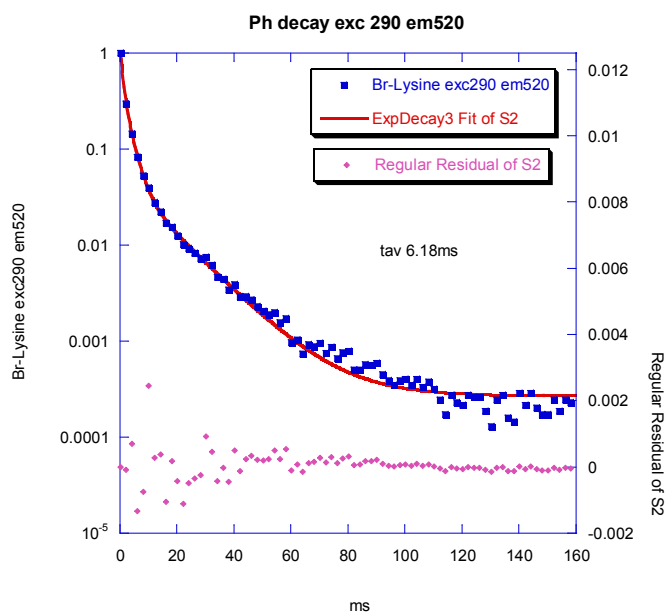
Fig.S21 Ph time decay of Lysine Br salt, exc 290nm emission 520nm
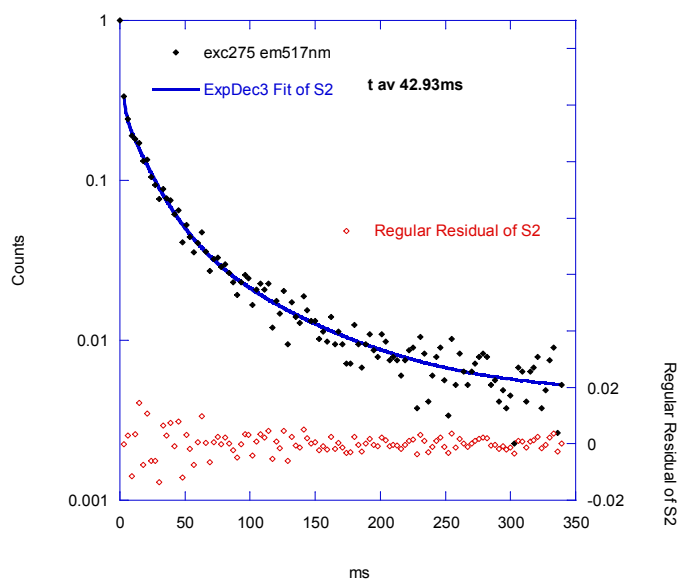
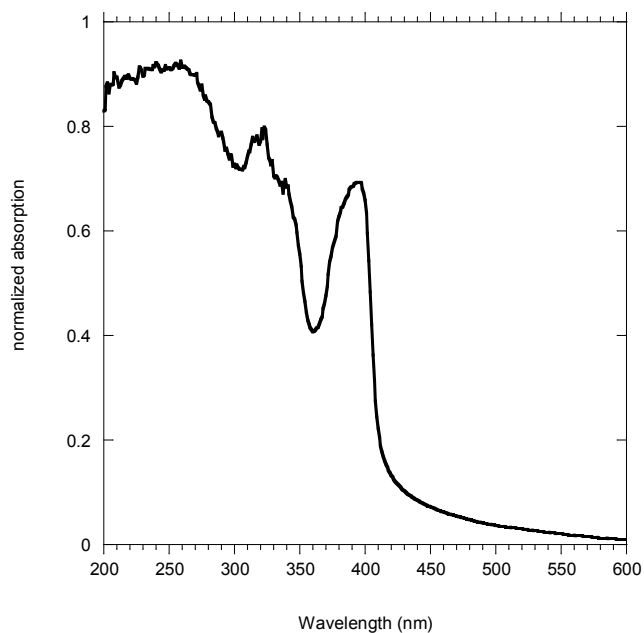Fig.S22 Ph time decay of Ornithine Cl salt, exc275nm, emission at 517nm

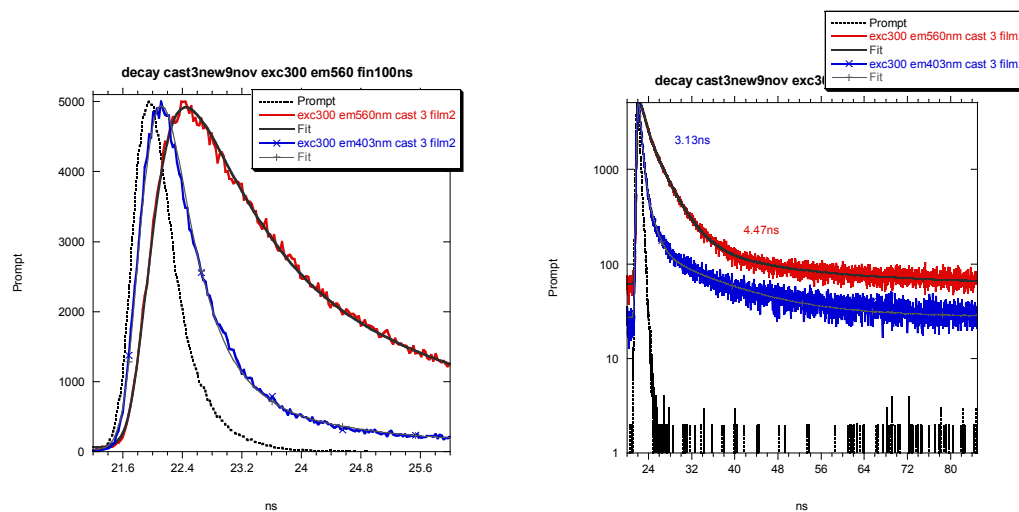Fig.S23 Optical absorption of cast film of compound **2**

Fig.S24 PL time decay of film of compound **2** , RT, exc300nm. Emission 403nm <τ>=0.35ns, τ_{av} = 3.13 ns; Emission 560nm <τ>=1.96ns, τ_{av} = 4.77 ns
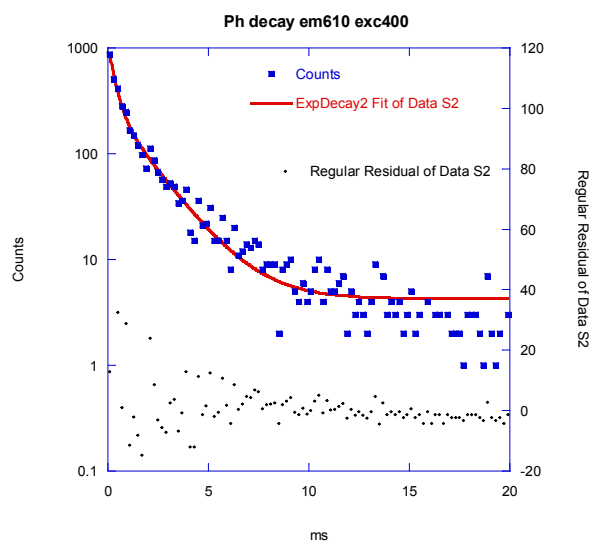
Fig.S25 Ph time decay of cast film of compound **2** , RT exc400nm, em610nm. τ_{av} = 1.26 ms;
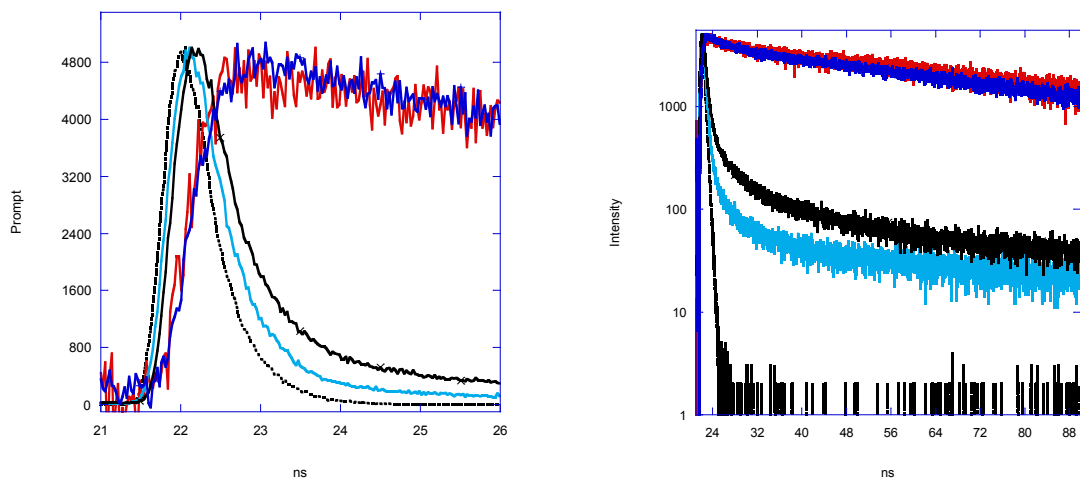

Fig.S26 PL time decay of cast film of compound **2** at different temperatures. T=845K, emission at 620nm and 403nm, red and cyano lines, respectively; T=132K, emission at 620nm and 403nm, blue and black lines, respectively. exc300nm.
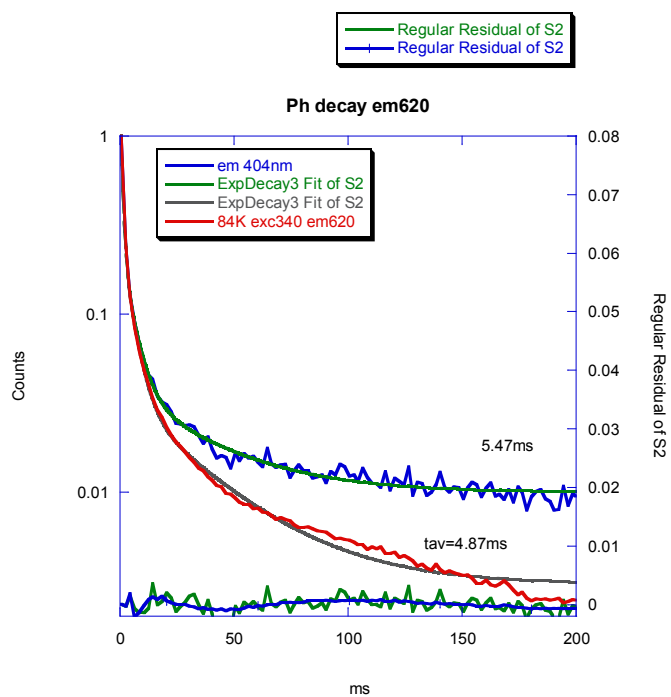
Fig.S27 Ph time decay of cast film of compound **2** at LT, exc300nm. Emission 404 nm τ_{av} = 5.47 ms; Emission 620 nm τ_{av} = 4.87 ms.