Supplementary file

Yttrium and lanthanide complexes of β-dialdehydes: synthesis, characterization, luminescence and electrochemistry of coordination compounds with the conjugate base of bromomalonaldehyde

Characterization data for the complexes

Characterization of ***6^{Y}***

$C_{36}H_{28}AsBr_4O_8Y$: calcd. C 40.3, H 2.63, Br 29.8; found C 40.5, H 2.65, Br 30.0. $\Lambda_M(H_2O)$: 63 Ω^{-1} mol^{-1} cm^2. IR (KBr): ν_{CO} = 1588-1561 cm^{-1}. UV-VIS (H_2O, 298 K, nm, max): 274. ^{1}H NMR ($(CD_3)_2SO$, 298 K, δ): 8.56 (s, 8H, *BrMA-H*); 8.00-7.55 (m, 20H, *$AsPh_4$*).

Characterization of ***6^{Eu}***

$C_{36}H_{28}AsBr_4O_8Eu$: calcd. C 38.1, H 2.49, Br 28.2; found C 38.3, H 2.50, Br 28.4. $\Lambda_M(H_2O)$: 64 Ω^{-1} mol^{-1} cm^2. IR (KBr): ν_{CO} = 1587-1560 cm^{-1}. UV-VIS (H_2O, 298 K, nm, max): 277. ^{1}H NMR (D_2O, 298 K, δ): 8.26 (s, 8H, *BrMA-H*); 7.80-7.45 (m, 20H, *$AsPh_4$*). PL (solid sample, λ_{exc} = 320 nm, 298 K, nm): 586, 592 ($^5D_0 \rightarrow {}^7F_1$); 611, 621 ($^5D_0 \rightarrow {}^7F_2$); 650, 657 ($^5D_0 \rightarrow {}^7F_3$); 692, 702 ($^5D_0 \rightarrow {}^7F_4$); 400-750 (*ligand emission*). Emission decay time (solid sample, 298 K): τ_1 = 0.383 ms (λ_{exc} = 320 nm, λ_{em} = 613 nm). Q_i = 9 %. τ_2 = 58 μs.

Characterization of ***6^{Tb}***

$C_{36}H_{28}AsBr_4O_8Tb$: calcd. C 37.9, H 2.47, Br 28.0; found C 38.0, H 2.50, Br 27.9. $\Lambda_M(H_2O)$: 59 Ω^{-1} mol^{-1} cm^2. IR (KBr): ν_{CO} = 1587-1559 cm^{-1}. UV-VIS (H_2O, 298 K, nm, max): 276. ^{1}H NMR (D_2O, 298 K, δ): 9.67 (s, slightly br, 8H, *BrMA-H*); 7.85-7.30 (m, 20H, *$AsPh_4$*). ^{1}H NMR (D_2O, 333 K, δ): 11.29 (s, slightly br, 8H, *BrMA-H*); 8.45-7.45 (m, 20H, *$AsPh_4$*). PL (solid sample, λ_{exc} = 320 nm, 298 K, nm): 488, 493 ($^5D_4 \rightarrow {}^7F_6$); 542, 548 ($^5D_0 \rightarrow {}^7F_5$); 582, 592 ($^5D_0 \rightarrow {}^7F_4$); 617, 621 ($^5D_0 \rightarrow {}^7F_3$); 400-750 (*ligand emission*). Emission decay time (solid sample, 298 K): τ_1 = 97 μs (λ_{exc} = 377 nm, λ_{em} = 544 nm). τ_2 = 58 μs.

Characterization of ***7^{Y}***

$C_{19}H_{14}Br_3N_2O_8Y$: calcd. C 31.4, H 1.94, N 3.85, Br 33.0; found C 31.5, H 2.00, N 3.85. IR (KBr): ν_{CO} = 1547 cm^{-1}. UV-VIS (H_2O, 298 K, nm, max): 276. ^1H NMR ($(CD_3)_2SO$, 298 K, δ): 8.66 (s, 6H, *BrMA-H*); 8.43 (d, 2H, $^3J_{HH}$ = 5.9 Hz, *bipyO$_2$-H$_6$-H$_6$'*); 7.83-7.52 (m, 6H, *bipyO$_2$-H$_3$-H$_3$'-H$_4$-H$_4$'-H$_5$-H$_5$'*).

Characterization of ***7^{Eu}***

$C_{19}H_{14}Br_3N_2O_8Eu$: calcd. C 28.9, H 1.79, N 3.55, Br 30.3; found C 29.1, H 1.80, N 3.55, Br 30.4. IR (KBr): ν_{CO} = 1549 cm^{-1}. UV-VIS (H_2O, 298 K, nm, max): 275. ^1H NMR ($(CD_3)_2SO$, 298 K, δ): 8.29 (d, 2H, $^3J_{HH}$ = 6.4 Hz, *bipyO$_2$-H$_6$-H$_6$'*); 7.75 (t, 2H, $^3J_{HH}$ = 7.9 Hz, *bipyO$_2$-H$_4$-H$_4$'*); 7.60-7.40 (m, 4H, *bipyO$_2$-H$_3$-H$_3$'-H$_5$-H$_5$'*); 4.77 (s, br, 6H, *BrMA-H*). ^1H NMR ($(CD_3)_2SO$, 314 K, δ): 8.32 (d, 2H, $^3J_{HH}$ = 6.4 Hz, *bipyO$_2$-H$_6$-H$_6$'*); 7.70 (t, 2H, $^3J_{HH}$ = 7.9 Hz, *bipyO$_2$-H$_4$-H$_4$'*); 7.60-7.40 (m, 4H, *bipyO$_2$-H$_3$-H$_3$'-H$_5$-H$_5$'*); 5.15 (s, br, 6H, *BrMA-H*). PL (solid sample, λ_{exc} = 320 nm, 298 K, nm): 584, 591 ($^5D_0 \rightarrow {}^7F_1$); 611, 616 ($^5D_0 \rightarrow {}^7F_2$); 649, 653 ($^5D_0 \rightarrow {}^7F_3$); 690, 699 ($^5D_0 \rightarrow {}^7F_4$). PLE (solid sample, λ_{em} = 611 nm, 298 K, nm): 325 (*ligand excitation*); 393, 415, 438, 464 (*Eu^{3+} excitation*). Emission decay time (solid sample, 298 K): τ = 0.096 ms (λ_{exc} = 320 nm, λ_{em} = 613 nm). Q_i = 5%.

Characterization of ***7^{Tb}***

$C_{19}H_{14}Br_3N_2O_8Tb$: calcd. C 28.6, H 1.77, N 3.52, Br 30.1; found C 28.7, H.1.80, N 3.55, Br 30.1. IR (KBr): ν_{CO} = 1549 cm^{-1}. UV-VIS (H_2O, 298 K, nm, max): 277. ^1H NMR ($(CD_3)_2SO$, 298 K, δ): 53.0 (s, very br, 6H, *BrMA-H*); 17.0 (s, br, 2H, *bipyO$_2$-H$_6$-H$_6$'*); 7.88, 7.44, 7.34 (3s, slightly br, 6H, *bipyO$_2$-H$_3$-H$_3$'- H$_4$-H$_4$'-H$_5$-H$_5$'*). ^1H NMR ($(CD_3)_2SO$, 314 K, δ): 48.2 (s, very br, 6H, *BrMA-H*); 14.9 (s, br, 2H, *bipyO$_2$-H$_6$-H$_6$'*); 8.00, 7.69, 7.52 (3s, slightly br, 6H, *bipyO$_2$-H$_3$-H$_3$'- H$_4$-H$_4$'-H$_5$-H$_5$'*). PL (solid sample, λ_{exc} = 286 nm, 298 K, nm): 488, 494 ($^5D_4 \rightarrow {}^7F_6$); 544, 547 ($^5D_4 \rightarrow {}^7F_5$); 581, 588 ($^5D_4 \rightarrow {}^7F_4$); 617, 621 ($^5D_4 \rightarrow {}^7F_3$). Emission decay time (solid sample, 298 K): τ = 18 μs (λ_{exc} = 320 nm, λ_{em} = 544 nm).

Characterization of ***8^{Y}***

$C_{21}H_{14}Br_3N_2O_6Y$: calcd. C 35.1, H 1.96, N 3.90, Br 33.3; found C 35.3, H 2.00, N 3.90, Br 33.5. IR (KBr): ν_{CO} = 1541 cm^{-1}. UV-VIS (H_2O, 298 K, nm, max): 264. ^1H NMR ($(CD_3)_2SO$, 306 K, δ): 9.13 (dd, 2H, $^3J_{HH}$ = 4.5 Hz, $^4J_{HH}$ = 1.8 Hz, *phen-H$_2$-H$_9$*); 8.66 (s, 6H, *BrMA-H*); 8.52 (dd, 2H, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.8 Hz, *phen-H$_4$-H$_7$*); 8.01 (s, 2H, *phen-H$_5$-H$_6$*); 7.79 (m, dd, 2H, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 4.5 Hz, *phen-H$_3$-H$_8$*).

Characterization of ***8^{Eu}***

$C_{21}H_{14}Br_3N_2O_6Eu$: calcd. C 32.3, H 1.80, N 3.58, Br 30.7; found C 32.5, H 1.80, N 3.60, Br 30.8. IR (KBr): ν_{CO} = 1540 cm^{-1}. UV-VIS (H_2O, 298 K, nm, max): 274. UV-VIS (CH_2Cl_2, 298 K, nm, max): 264. ^{1}H NMR ($(CD_3)_2SO$, 298 K, δ): 8.95 (s, very br, 2H, *phen-H$_2$-H$_9$*); 8.55 (d, 2H, $^3J_{HH}$ = 8.0 Hz, *phen-H$_4$-H$_7$*); 8.01 (s, 2H, *phen-H$_5$-H$_6$*); 7.64 (m, slightly br, 2H, *phen-H$_3$-H$_8$*); 4.47 (s, slightly br, 6H, *BrMA-H*). ^{1}H NMR ($(CD_3)_2SO$, 324 K, δ): 8.51 (d, 2H, $^3J_{HH}$ = 8.3 Hz, *phen-H$_4$-H$_7$*); 8.48 (s, very br, 2H, *phen-H$_2$-H$_9$*); 7.97 (s, 2H, *phen-H$_5$-H$_6$*); 7.63 (dd, 2H, $^3J_{HH}$ = 8.3 Hz, $^3J_{HH}$ = 4.3 Hz, *phen-H$_3$-H$_8$*); 5.01 (s, slightly br, 6H, *BrMA-H*). PL (solid sample, λ_{exc} =320 nm, 298 K, nm): 589, 593 ($^5D_0 \rightarrow {}^7F_1$); 611, 621 ($^5D_0 \rightarrow {}^7F_2$); 651 ($^5D_0 \rightarrow {}^7F_3$); 696, 700-702 ($^5D_0 \rightarrow {}^7F_4$). Emission decay time (solid sample, 298 K): τ = 0.224 ms (λ_{exc} = 320 nm, λ_{em} = 613 nm). Q_i = 12 %.

Characterization of ***8^{Tb}***

$C_{21}H_{14}Br_3N_2O_6Tb$: calcd. C 32.0, H 1.79, N 3.55, Br 30.4; found C 32.1, H 1.80, N 3.55, Br 30.5. IR (KBr): ν_{CO} = 1540 cm^{-1}. UV-VIS (H_2O, 298 K, nm, max): 275. UV-VIS (CH_2Cl_2, 298 K, nm, max): 268. ^{1}H NMR ($(CD_3)_2SO$, 298 K, δ): 60.7 (s, very br, 6H, *NMA-H*); 10.65-6.05 (m, very br, 8H, *phen*). ^{1}H NMR ($(CD_3)_2SO$, 328 K, δ): 52.1 (s, very br, 6H, *NMA-H*); 9.65-4.00 (m, very br, 8H, *phen*). PL (solid sample, λ_{exc} = 320 nm, 298 K, nm): 489, 495 ($^5D_4 \rightarrow {}^7F_6$); 543, 549 ($^5D_4 \rightarrow {}^7F_5$); 581, 585 ($^5D_4 \rightarrow {}^7F_4$); 617, 621 ($^5D_4 \rightarrow {}^7F_3$). Emission decay time (solid sample, 298 K): τ = 51 μs (λ_{exc} = 320 nm, λ_{em} = 544 nm).

Characterization of ***9^{Y}***

$C_{24}H_{17}Br_3N_3O_6Y$: calcd. C 37.3, H 2.22, N 5.44, Br 31.1; found C 37.4, H 2.25, N 5.45, Br 31.2. IR (KBr): ν_{CO} = 1553 cm^{-1}. UV-VIS (H_2O, 298 K, nm, max): 278. ^{1}H NMR ($(CD_3)_2SO$, 298 K, δ): 8.72 (d, 2H, $^3J_{HH}$ = 4.8 Hz, *terpy-H$_6$-H$_6$''*); 8.70 (s, 6H, *BrMA-H*); 8.61 (d, 2H, $^3J_{HH}$ = 8.0 Hz, *terpy-H$_3$-H$_3$''*); 8.44 (d, 2H, $^3J_{HH}$ = 7.8 Hz, *terpy-H$_3$'-H$_5$'*); 8.09 (t, 1H, $^3J_{HH}$ = 7.8 Hz, *terpy-H$_4$'*); 8.00 (td, 2H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.7 Hz, *terpy-H$_4$-H$_4$''*); 7.48 (dd, 2H, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 4.8 Hz, *terpy-H$_5$-H$_5$''*).

Characterization of ***9^{Eu}***

$C_{24}H_{17}Br_3N_3O_6Eu$: calcd. C 34.5, H 2.05, N 5.03, Br 28.7; found C 34.7, H 2.05, N 5.05, Br 28.8. IR (KBr): ν_{CO} = 1550 cm^{-1}. UV-VIS (H_2O, 298 K, nm, max): 278. ^{1}H NMR ($(CD_3)_2SO$, 298 K, δ): 8.72 (d, 2H, $^3J_{HH}$ = 4.8 Hz, *terpy-H$_6$-H$_6$''*); 8.62 (d, 2H, $^3J_{HH}$ = 8.0 Hz, *terpy-H$_3$-H$_3$''*); 8.45 (d, 2H, $^3J_{HH}$ = 7.8 Hz, *terpy-H$_3$'-H$_5$'*); 8.10 (t, 1H, $^3J_{HH}$ = 7.8 Hz, *terpy-H$_4$'*); 8.00 (td, 2H, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.7 Hz, *terpy-H$_4$-*

H₄''); 7.49 (dd, 2H, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 4.8 Hz, *terpy-H₅-H₅''*); 4.92 (s, 6H, *BrMA-H*). *BrMA-H* signal fall at 5.33 ppm at 320 K. PL (solid sample, λ_{exc} = 320 nm, 298 K, nm): 592 ($^5D_0 \rightarrow {}^7F_1$); 614, 618 ($^5D_0 \rightarrow {}^7F_2$); 649 ($^5D_0 \rightarrow {}^7F_3$); 688, 693-698 ($^5D_0 \rightarrow {}^7F_4$). Emission decay time (solid sample, 298 K): τ = 0.772 ms (λ_{exc} = 320 nm, λ_{em} = 613 nm). Q_i = 34%.

Characterization of ***9^{Tb}***

$C_{24}H_{17}Br_3N_3O_6Eu$: calcd. C 34.2, H 2.03, N 4.99, Br 28.5; found C 34.4, H 2.05, N 5.00, Br 28.6. IR (KBr): ν_{CO} = 1545 cm^{-1}. UV-VIS (H_2O, 298 K, nm, max): 278. ^{1}H NMR ($(CD_3)_2SO$, 298 K, δ): 65.7 (s, very br, 6H, *BrMA-H*); 9.05-8.72 (m, slightly br, 4H, *terpy*); 8.59 (d, 2H, $^3J_{HH}$ = 7.4 Hz, *terpy*); 8.32-7.97 (m, 3H, *terpy*); 7.64 (m, slightly br, 2H, *terpy*). *BrMA-H* signal fall at 52.7 ppm at 333 K. PL (solid sample, λ_{exc} = 320 nm, 298 K, nm): 488, 492 ($^5D_4 \rightarrow {}^7F_6$); 542, 548 ($^5D_4 \rightarrow {}^7F_5$); 582, 589 ($^5D_4 \rightarrow {}^7F_4$); 619, 622 ($^5D_4 \rightarrow {}^7F_3$). Emission decay time (solid sample, 298 K): τ = 11 μs (λ_{exc} = 320 nm, λ_{em} = 544 nm).

Characterization data for the ionic liquids

Characterization of ***[P$_{\&\&\&1}$][BrMA]***

$C_{28}H_{56}BrO_2P$: calcd. C 62.8, H 10.5, Br 14.9; found C 62.9, H 10.6, Br 14.8. IR: ν_{CO} = 1567 cm^{-1}. ^{1}H NMR ($CDCl_3$, 298 K, δ): 8.81 (s, 2H, *BrMA-H*); 2.23 (m, 6H, *P-CH₂*); 1.91 (d, 3H, $^2J_{PH}$ = 13.2 Hz, *P-CH₃*); 1.47, 1.25, 0.86 (3m, 45H, *octyl*). ^{31}P {^{1}H} NMR ($CDCl_3$, 298 K, δ): 32.1. PL (ionic liquid, λ_{exc} = 350 nm, 298 K, nm): 400-650, max 478. PLE (ionic liquid, λ_{em} = 480 nm, 298 K, nm): max 422. Emission decay time (ionic liquid, 298 K): τ = 1.6 ns (λ_{exc} = 373 nm, λ_{em} = 535 nm).

Characterization of ***Eu@[P$_{\&\&\&1}$][BrMA]***

^{1}H NMR ($CDCl_3$, 298 K, δ): 8.68 (s, slightly br, 2H, *BrMA-H*); 2.27 (m, 6H, *P-CH₂*); 1.95 (d, 3H, $^2J_{PH}$ = 13.2 Hz, *P-CH₃*); 1.47, 1.24, 0.85 (3m, 45H, *octyl*). ^{31}P {^{1}H} NMR ($CDCl_3$, 298 K, δ): 32.0.

Characterization of ***Tb@[P$_{\&\&\&1}$][BrMA]***

^{1}H NMR ($CDCl_3$, 298 K, δ): 9.04 (s, br, 2H, *BrMA-H*); 2.70-0.60 (m, 54H, *phosphonium hydrogen atoms*). ^{31}P {^{1}H} NMR ($CDCl_3$, 298 K, δ): 32.0.

Characterization data for the plastic materials

Characterization of ***7^{Eu}@PMMA***

PL (solid sample, λ_{exc} = 320 nm, 298 K, nm): 591 ($^5D_0 \rightarrow {}^7F_1$); 611, 617 ($^5D_0 \rightarrow {}^7F_2$); 650, 653 ($^5D_0 \rightarrow {}^7F_3$); 691, 700 ($^5D_0 \rightarrow {}^7F_4$). PLE (solid sample, λ_{em} = 611 nm, 298 K, nm): max 279 (*ligand excitation*); 393, 415, 464 (*Eu^{3+} excitation*). Emission decay time (solid sample, 298 K): τ = 0.127 ms (λ_{exc} = 320 nm, λ_{em} = 613 nm). Q_i = 5%.

Characterization of ***7^{Tb}@PMMA***

PL (solid sample, λ_{exc} = 280 nm, 298 K, nm): 489, 494 ($^5D_4 \rightarrow {}^7F_6$); 544 ($^5D_4 \rightarrow {}^7F_5$); 581, 588 ($^5D_4 \rightarrow {}^7F_4$); 617, 621 ($^5D_4 \rightarrow {}^7F_3$). PLE (solid sample, λ_{em} = 544 nm, 298 K, nm): max 280 (*ligand excitation*). Emission decay time (solid sample, 298 K): τ = 11 μs (λ_{exc} = 320 nm, λ_{em} = 544 nm).

Characterization of ***8^{Eu}@PMMA***

PL (solid sample, λ_{exc} =320 nm, 298 K, nm): 579 ($^5D_0 \rightarrow {}^7F_0$); 589, 593 ($^5D_0 \rightarrow {}^7F_1$); 611, 621 ($^5D_0 \rightarrow {}^7F_2$); 650, 654 ($^5D_0 \rightarrow {}^7F_3$); 689, 696-700 ($^5D_0 \rightarrow {}^7F_4$). PLE (solid sample, λ_{em} = 611 nm, 298 K, nm): max 334 nm (*ligand excitation*); 393, 400, 464 (*Eu^{3+} excitation*). Emission decay time (solid sample, 298 K): τ = 0.254 ms (λ_{exc} = 320 nm, λ_{em} = 613 nm). Q_i = 13 %.

Characterization of ***8^{Tb}@PMMA***

PL (solid sample, λ_{exc} = 280 nm, 298 K, nm): 490 ($^5D_4 \rightarrow {}^7F_6$); 542, 549 ($^5D_4 \rightarrow {}^7F_5$); 581, 585 ($^5D_4 \rightarrow {}^7F_4$); 612, 621 ($^5D_4 \rightarrow {}^7F_3$). PLE (solid sample, λ_{em} = 543 nm, 298 K, nm): max 334 (*ligand excitation*). Emission decay time (solid sample, 298 K): τ = 56 μs (λ_{exc} = 320 nm, λ_{em} = 544 nm).

Characterization of ***9^{Eu}@PMMA***

PL (solid sample, λ_{exc} =335 nm, 298 K, nm): 579 ($^5D_0 \rightarrow {}^7F_0$); 592 ($^5D_0 \rightarrow {}^7F_1$); 614, 618 ($^5D_0 \rightarrow {}^7F_2$); 650 ($^5D_0 \rightarrow {}^7F_3$); 688, 694-698 ($^5D_0 \rightarrow {}^7F_4$). PLE (solid sample, λ_{em} = 614 nm, 298 K, nm): max 330 (*ligand excitation*); 394, 416, 464 (*Eu^{3+} excitation*). Emission decay time (solid sample, 298 K): τ = 0.783 ms (λ_{exc} = 325 nm, λ_{em} = 613 nm). Q_i = 30 %.

Characterization of ***9^{Tb}@PMMA***

PL (solid sample, λ_{exc} = 310 nm, 298 K, nm): 488, 492 ($^5D_4 \rightarrow {}^7F_6$); 542, 548 ($^5D_4 \rightarrow {}^7F_5$); 582, 589 ($^5D_4 \rightarrow {}^7F_4$); 620, 622 ($^5D_4 \rightarrow {}^7F_3$). Emission decay time (solid sample, 298 K): τ = 12 μs (λ_{exc} = 320 nm, λ_{em} = 544 nm).

Characterization of ***Eu-BrMA@PVP***

PL (solid sample, λ_{exc} = 330 nm, 298 K, nm): 584, 591 ($^5D_0 \rightarrow {}^7F_1$); 614 ($^5D_0 \rightarrow {}^7F_2$); 652 ($^5D_0 \rightarrow {}^7F_3$); 688-700 ($^5D_0 \rightarrow {}^7F_4$). PLE (solid sample, λ_{em} = 613 nm, 298 K, nm): ≤ 340 nm (*ligand excitation*); 394, 417, 464 (*Eu^{3+} excitation*). Emission decay time (solid sample, 298 K): τ = 0.365 μs (λ_{exc} = 320 nm, λ_{em} = 613 nm). Q_i = 23 %.

Characterization of ***Tb-BrMA@PVP***

PL (solid sample, λ_{exc} = 320 nm, 298 K, nm): 488, 492 ($^5D_4 \rightarrow {}^7F_6$); 545 ($^5D_4 \rightarrow {}^7F_5$); 582, 589 ($^5D_4 \rightarrow {}^7F_4$); 618, 621 ($^5D_4 \rightarrow {}^7F_3$). PLE (solid sample, λ_{em} = 544 nm, 298 K, nm): ≤ 340 nm (*ligand excitation*). Emission decay time (solid sample, 298 K): τ = 14 μs (λ_{exc} = 320 nm, λ_{em} = 544 nm).