crystals

Extended π-Systems in Diimine Ligands in [Cu(P^P)(N^N)][PF6] Complexes: From 2,2'-Bipyridine to 2-(Pyridin-2-yl)Quinoline

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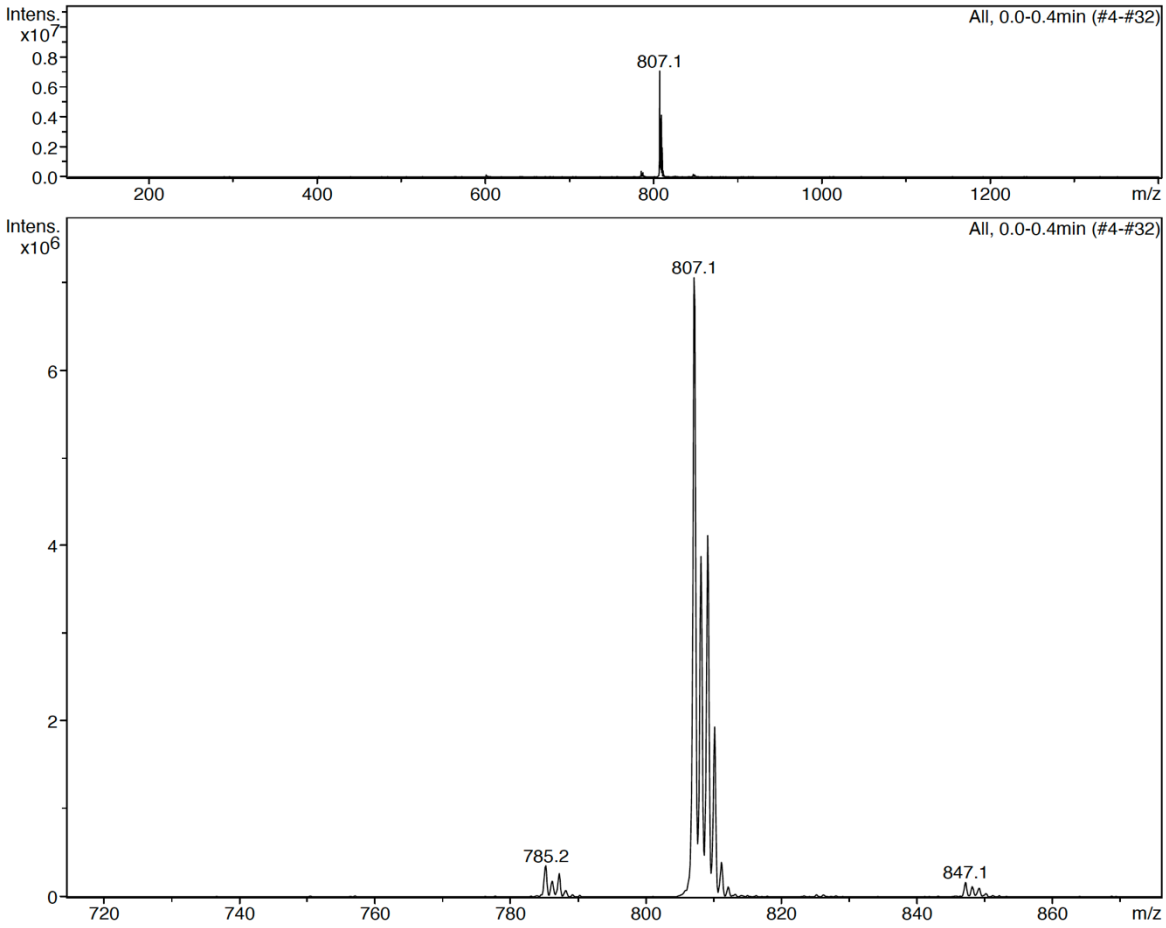
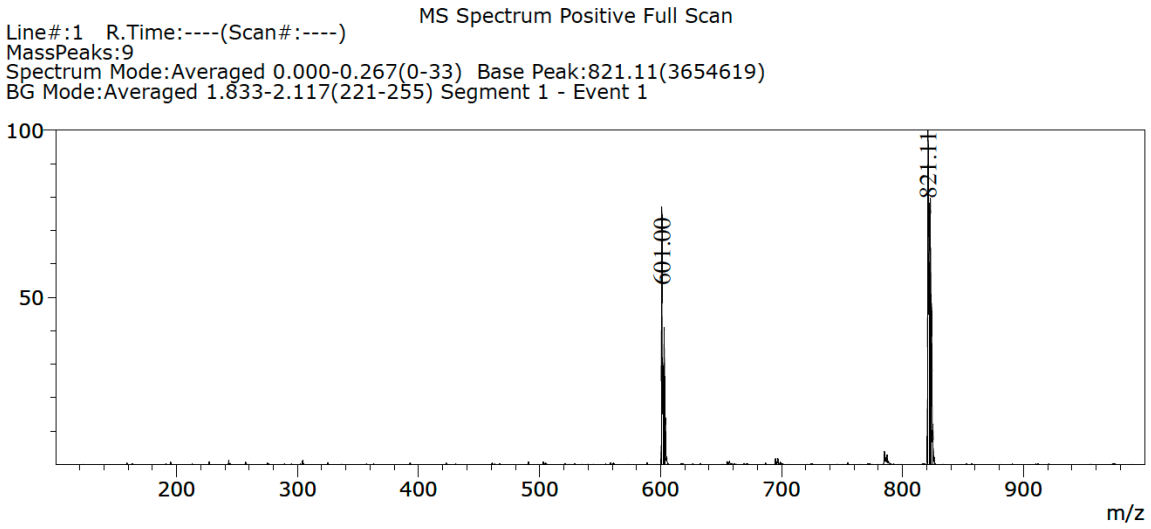
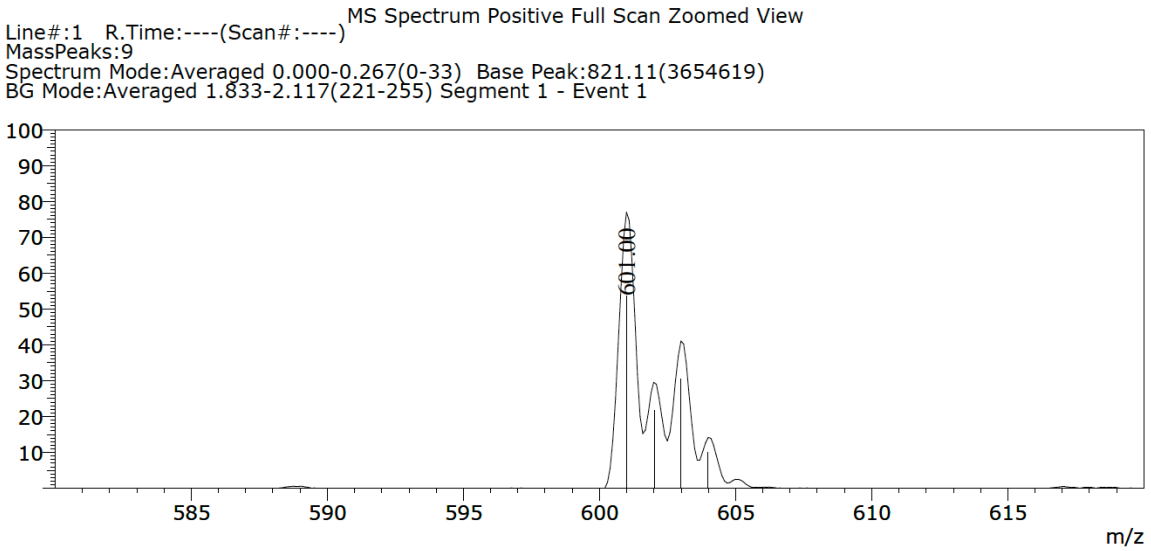


Figure S1. Electrospray mass spectrum of [Cu(POP)(**1**)][PF6], positive mode.





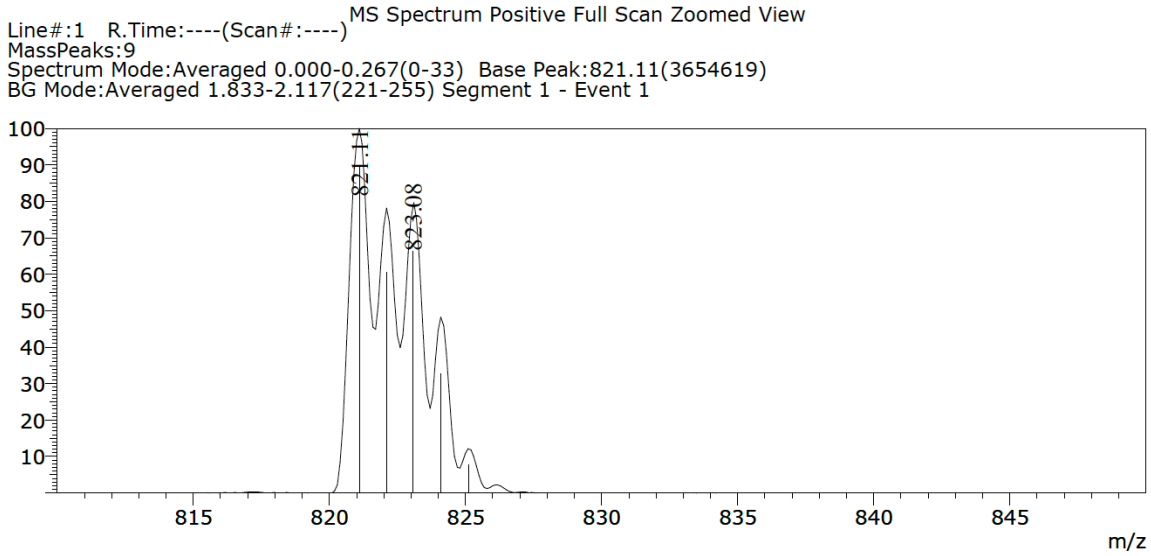


Figure S2. Electrospray mass spectrum of [Cu(POP)(**2**)][PF_6], positive mode.

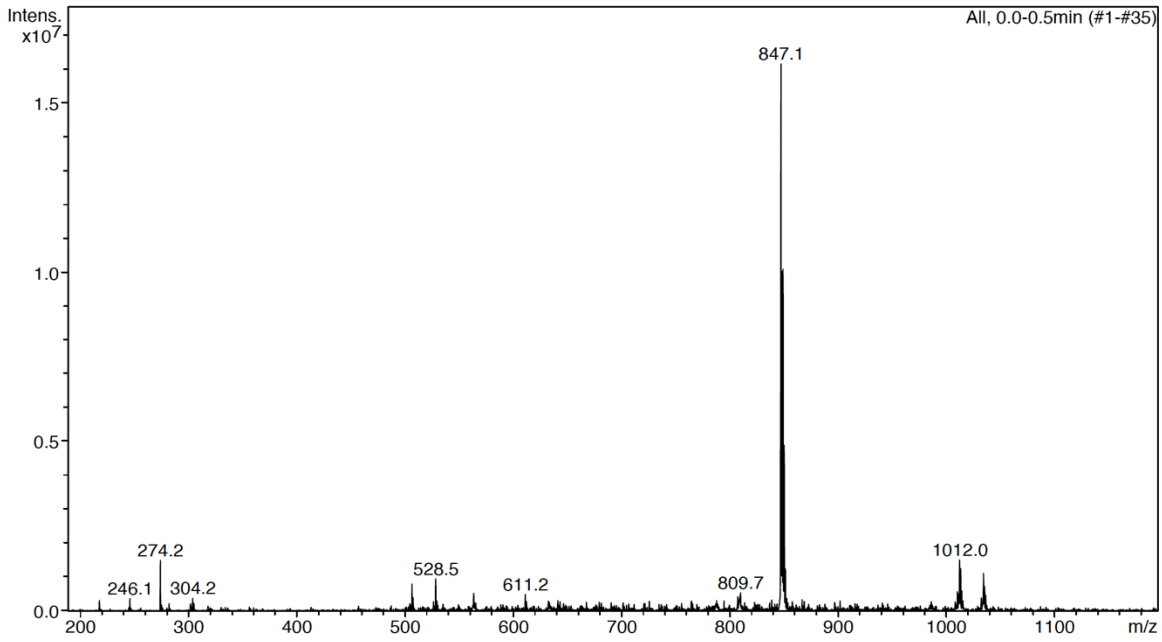


Figure S3. Electrospray mass spectrum of [Cu(xantphos)(**1**)][PF_6], positive mode.

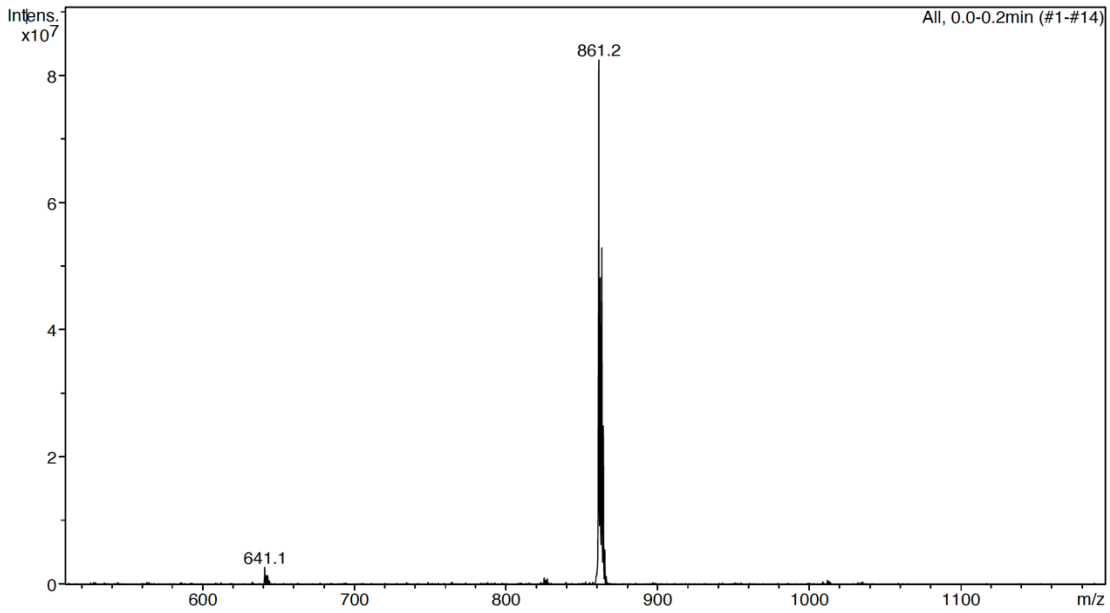


Figure S4. Electrospray mass spectrum of [Cu(xantphos)(**2**)][PF_6], positive mode.

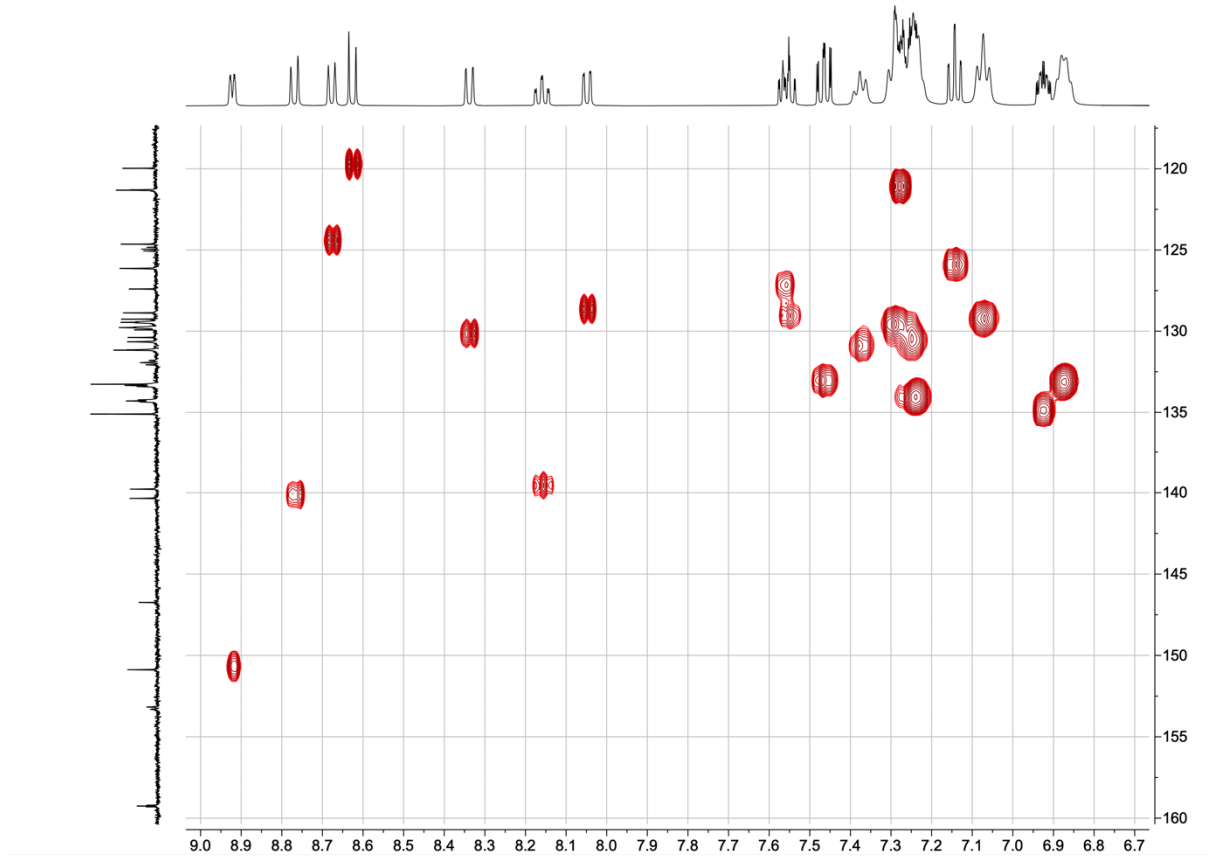


Figure S5. HMQC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C, 298 K, acetone-d_6) of [Cu(POP)(**1**)][PF_6].

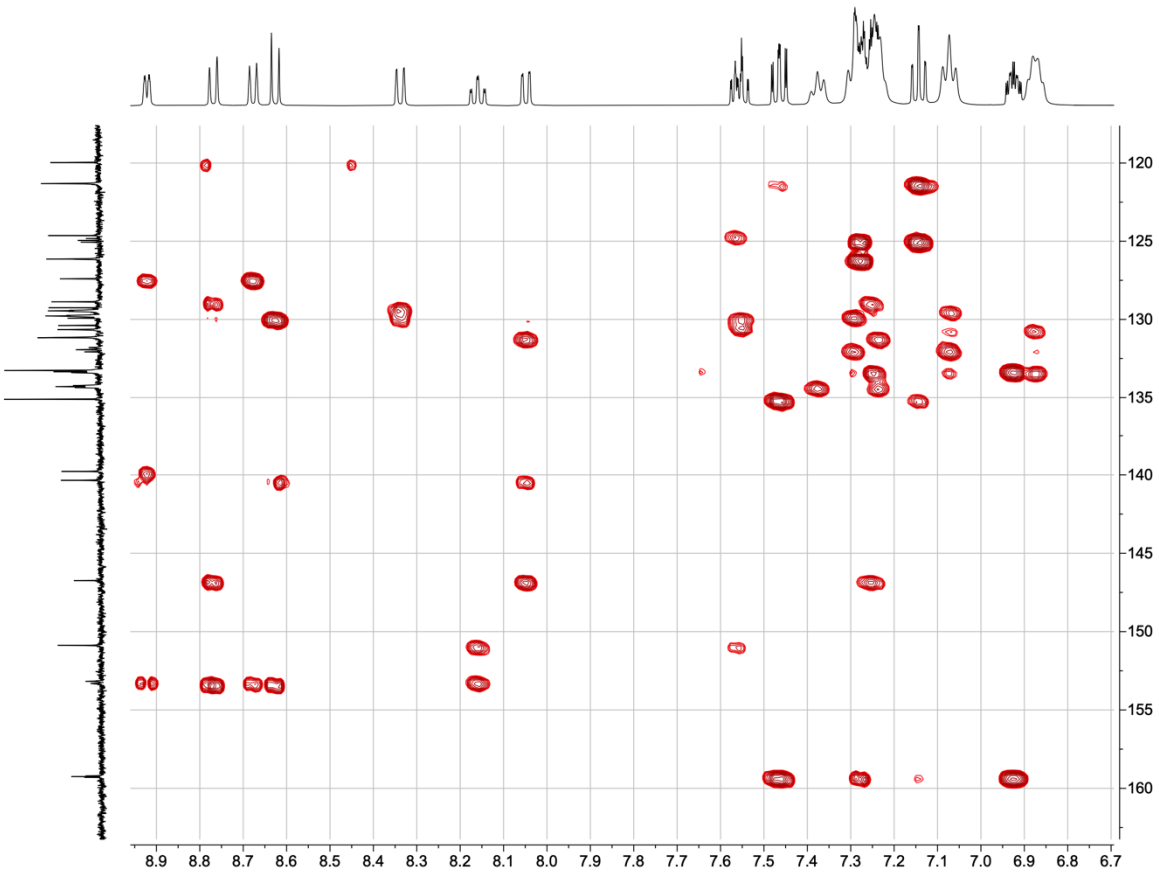


Figure S6. HMBC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C, 298 K, acetone-d_6) of [Cu(POP)(**1**)][PF_6].

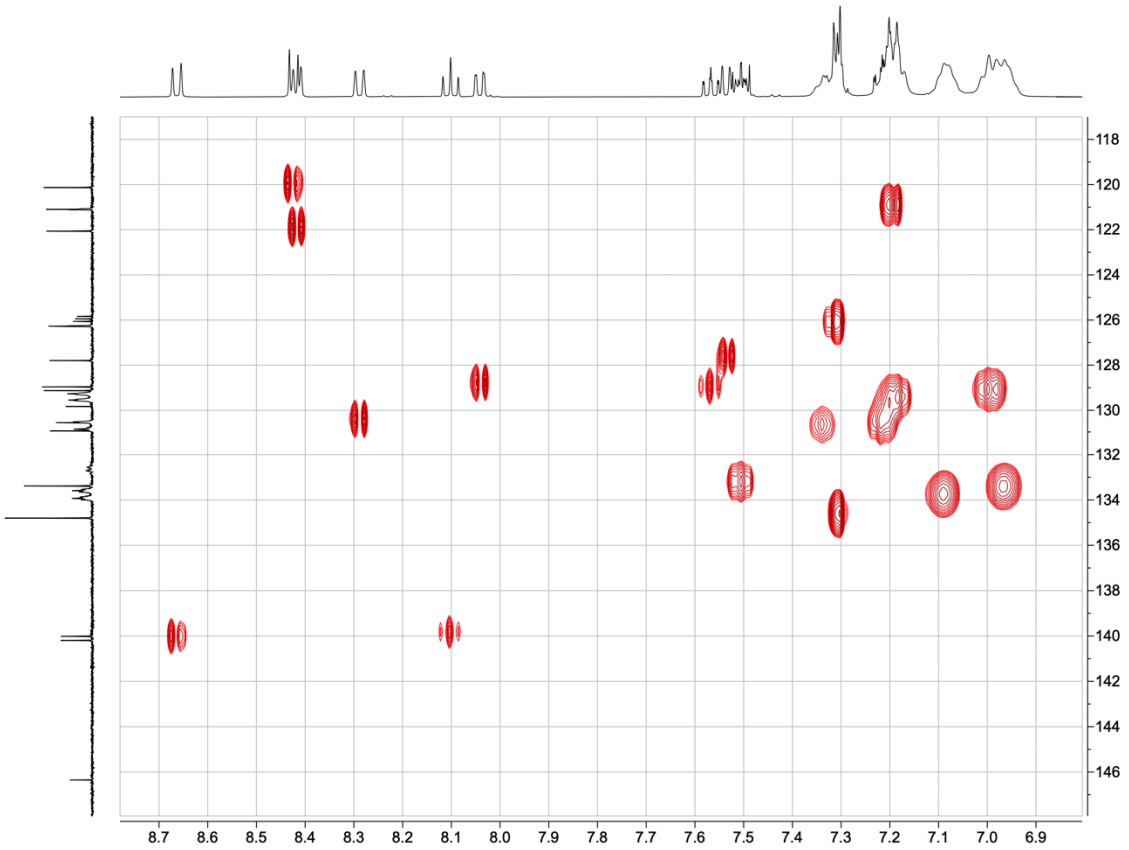


Figure S7. Aromatic region of the HMQC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C, 298 K, acetone-d_6) of [Cu(POP)(**2**)][PF_6].

Figure S8. Part of the HMBC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C, 298 K, acetone-d_6) of [Cu(POP)(**2**)][PF_6]. * = H_2O and HOD.

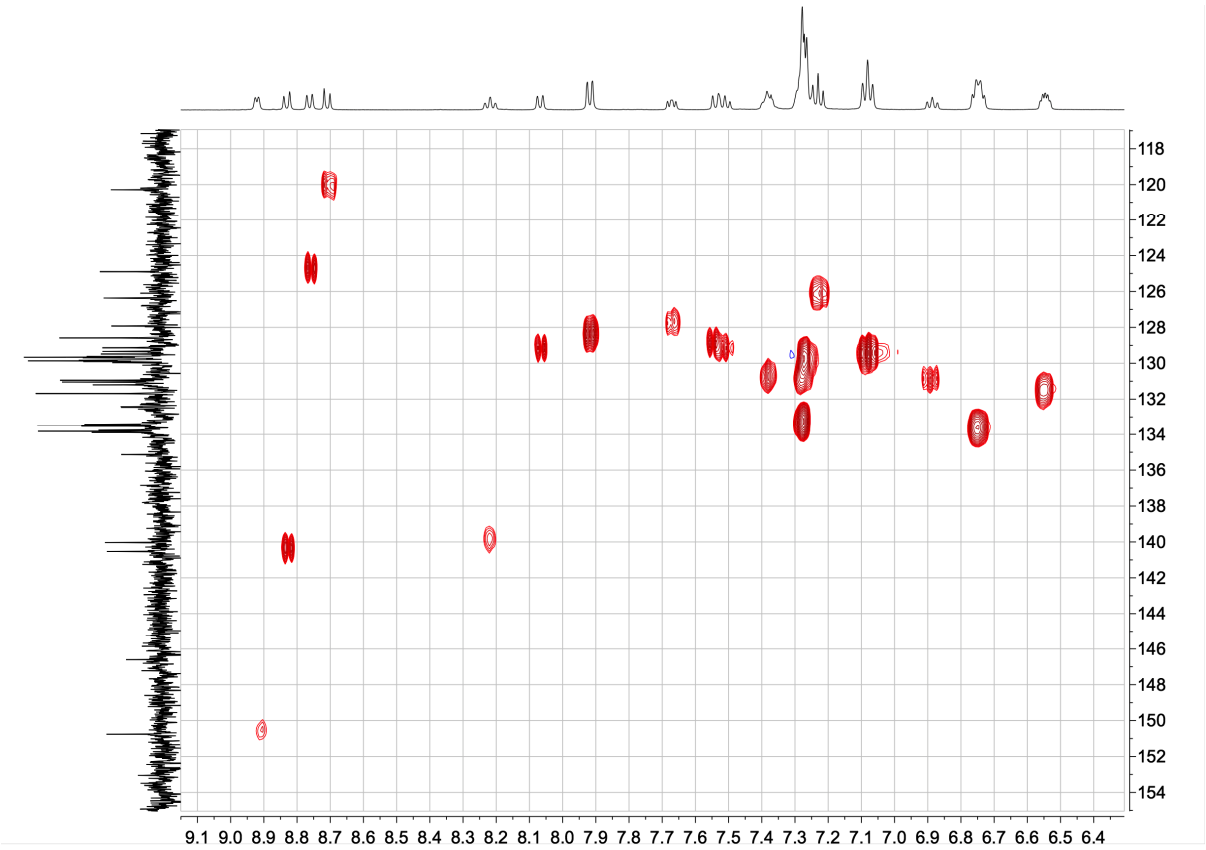


Figure S9. Part of the HMQC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C, 298 K, acetone-d_6) of [Cu(xantphos)(**1**)][PF_6].

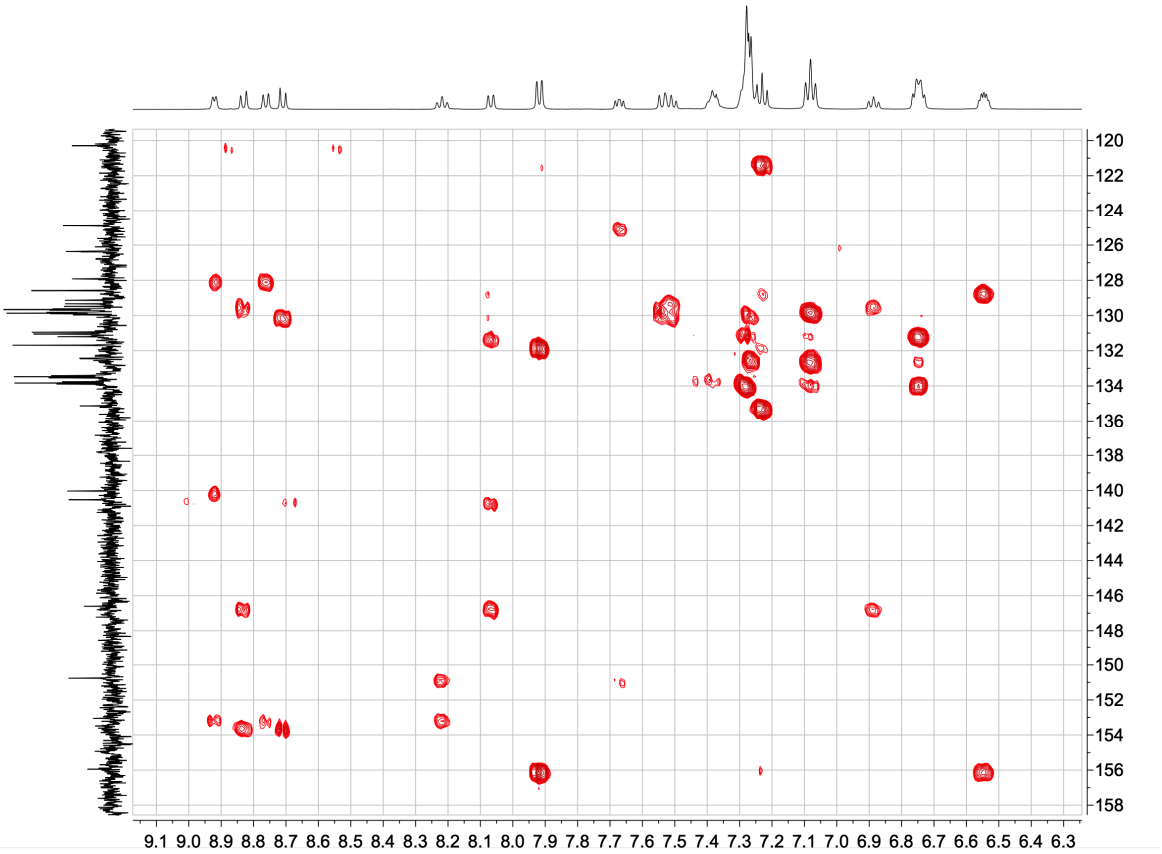


Figure S10. Part of the HMBC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C, 298 K, acetone-d_6) of [Cu(xantphos)(**1**)][PF_6].

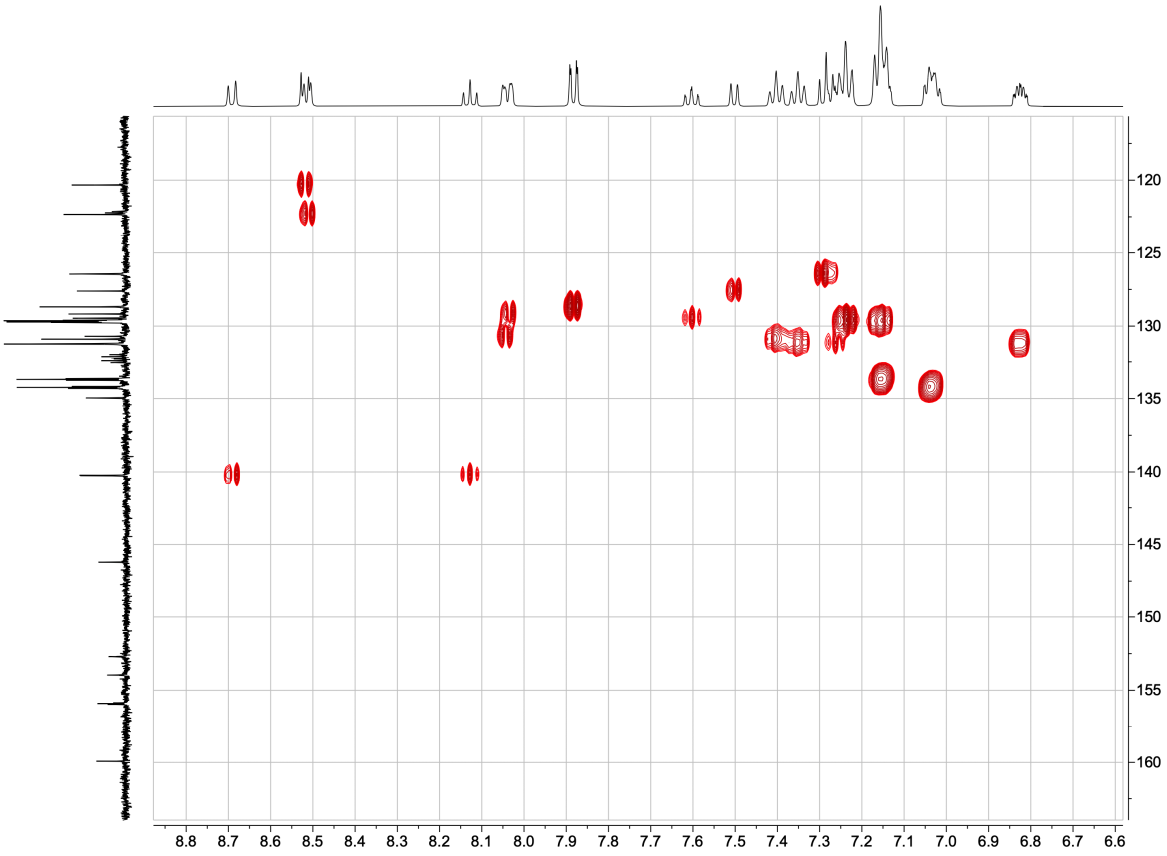


Figure S11. Part of the HMQC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C, 298 K, acetone-d_6) of [Cu(xantphos)(**2**)][PF_6]. .

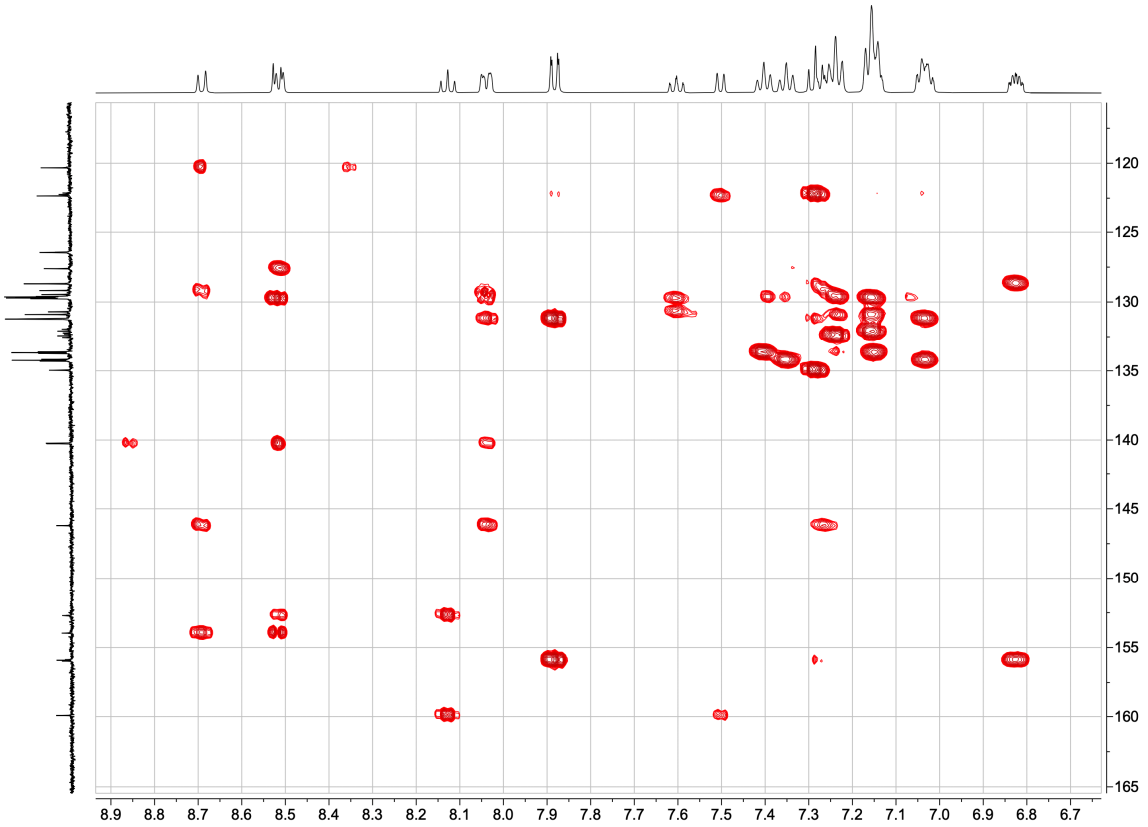


Figure S12. Part of the HMBC spectrum (500 MHz ^{1}H, 126 MHz ^{13}C, 298 K, acetone-d_6) of [Cu(xantphos)(**2**)][PF_6].

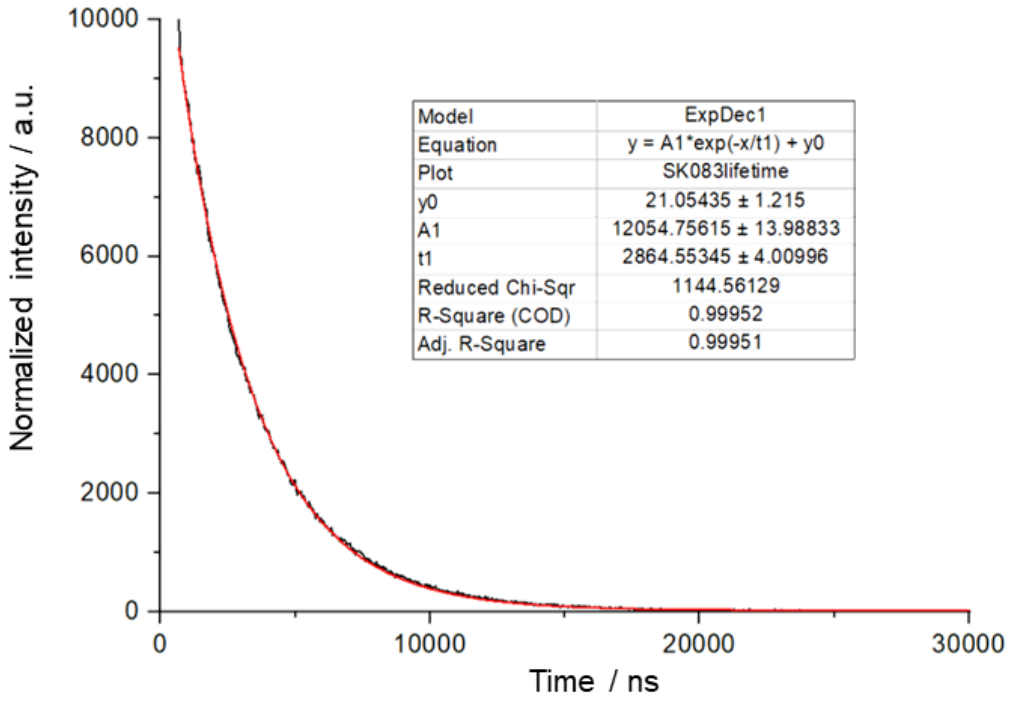


Figure S13. Solid-state lifetime decay (black) and first-order fitting curve (red) of [Cu(POP)(**1**)][PF_6] (λ_{exc} = 365 nm, exponential fitting done with Origin 2020).

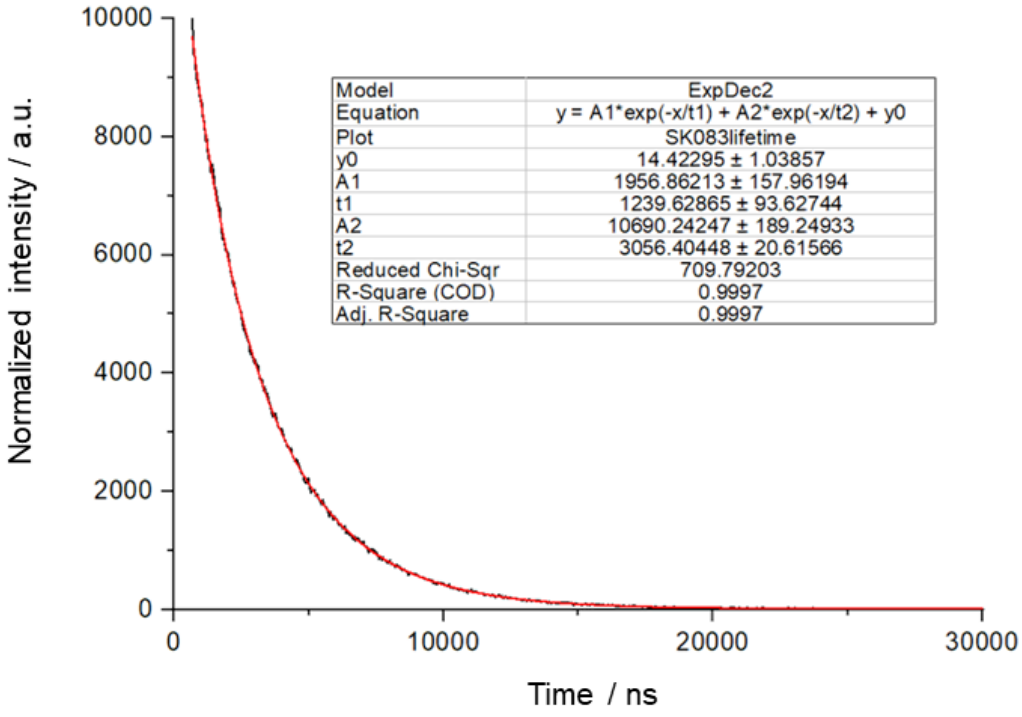


Figure S14. Solid-state lifetime decay (black) and second-order fitting curve (red) of [Cu(POP)(**1**)][PF_6] (λ_{exc} = 365 nm, exponential fitting done with Origin 2020).

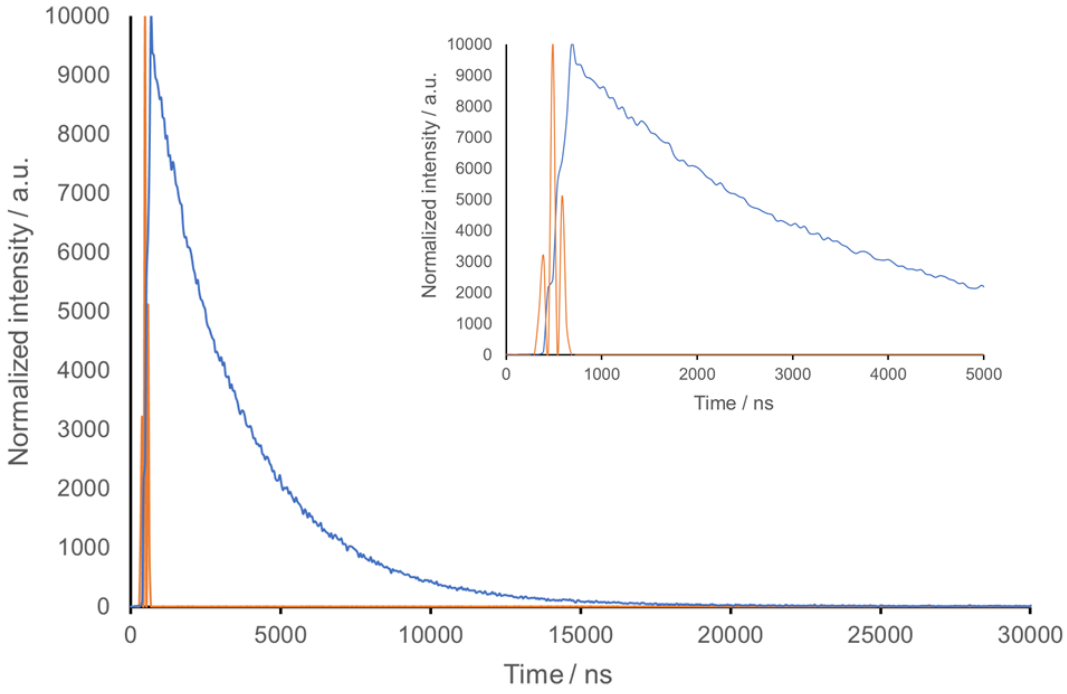


Figure S15. Solid-state lifetime decay of [Cu(POP)(**1**)][PF_6] (blue) and IRF (orange) (λ_{exc} = 365 nm).

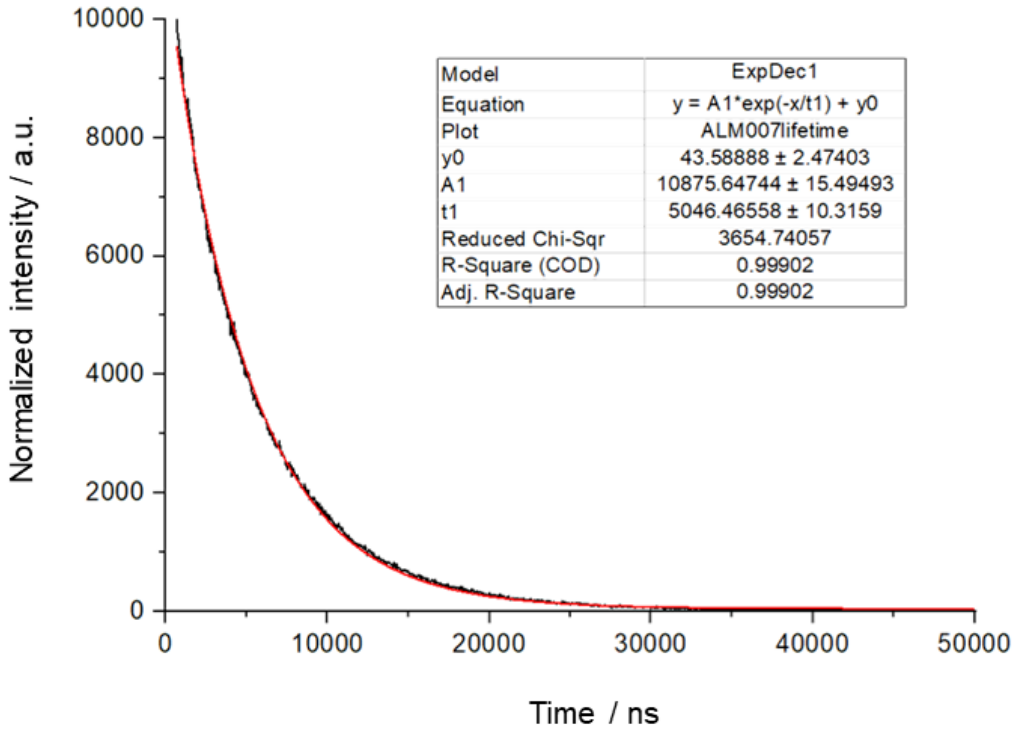


Figure S16. Solid-state lifetime decay (black) and first-order fitting curve (red) of [Cu(xantphos)(**1**)][PF_6] (λ_{exc} = 365 nm, exponential fitting done with Origin 2020).

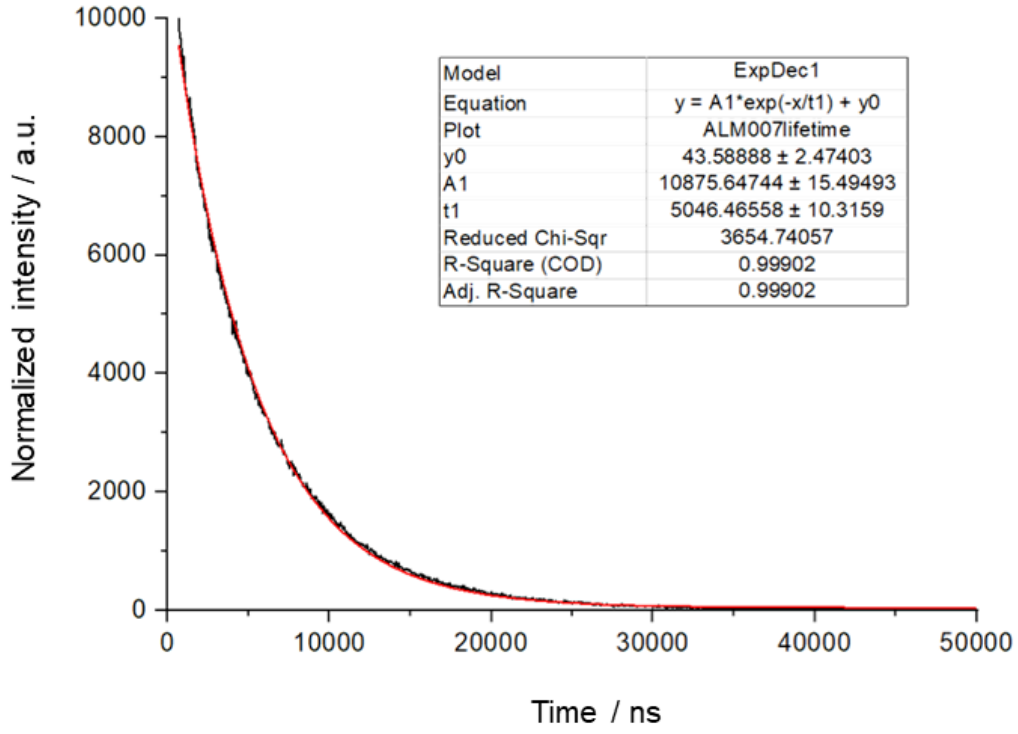


Figure S17. Solid-state lifetime decay (black) and second-order fitting curve (red) of [Cu(xantphos)(**1**)][PF_6] (λ_{exc} = 365 nm, exponential fitting done with Origin 2020).

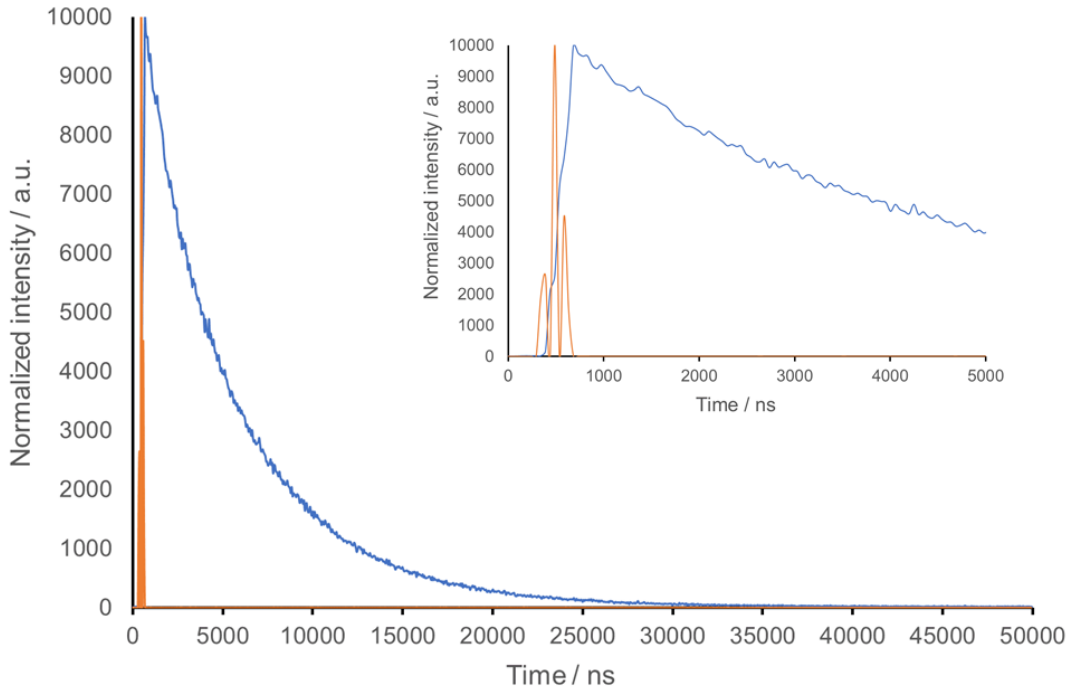


Figure S18. Solid-state lifetime decay of [Cu(xantphos)(**1**)][PF_6] (blue) and IRF (orange) (λ_{exc} = 365 nm).

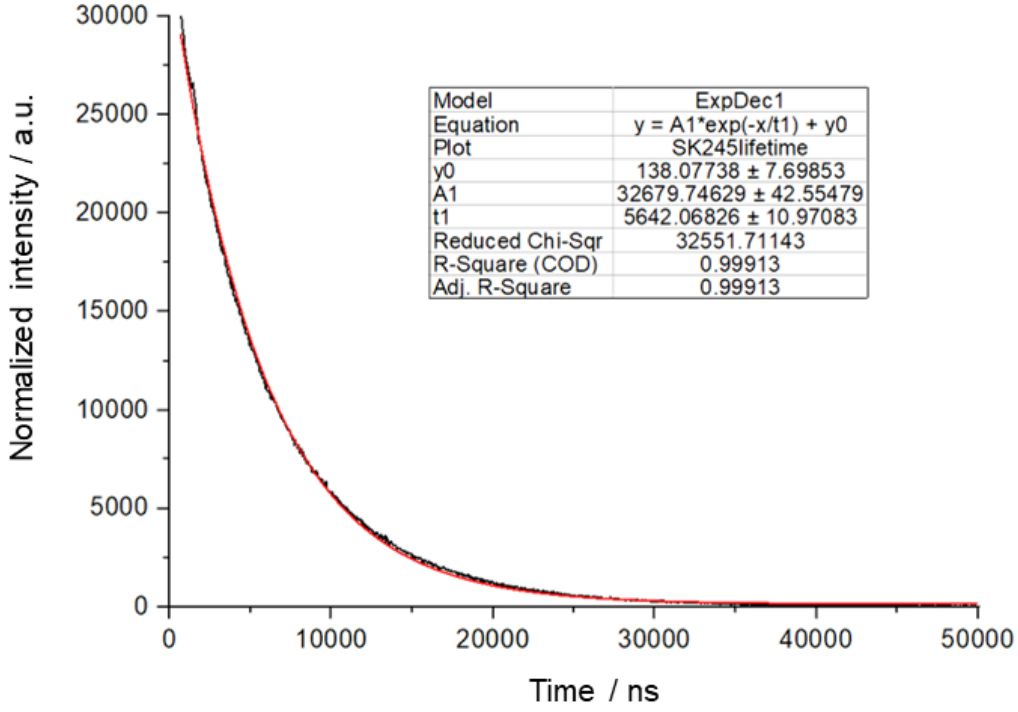


Figure S19. Solid-state lifetime decay (black) and first-order fitting curve (red) of [Cu(POP)(**2**)][PF_6] (λ_{exc} = 365 nm, exponential fitting done with Origin 2020).

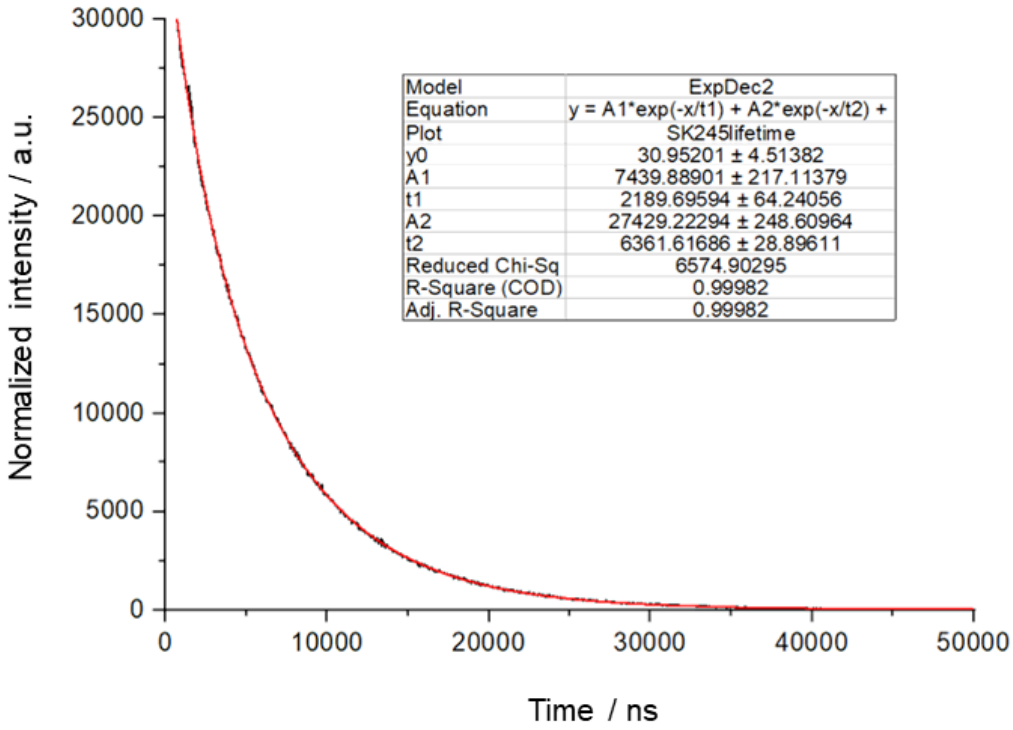


Figure S20. Solid-state lifetime decay (black) and second-order fitting curve (red) of [Cu(POP)(**2**)][PF_6] (λ_{exc} = 365 nm, exponential fitting done with Origin 2020).

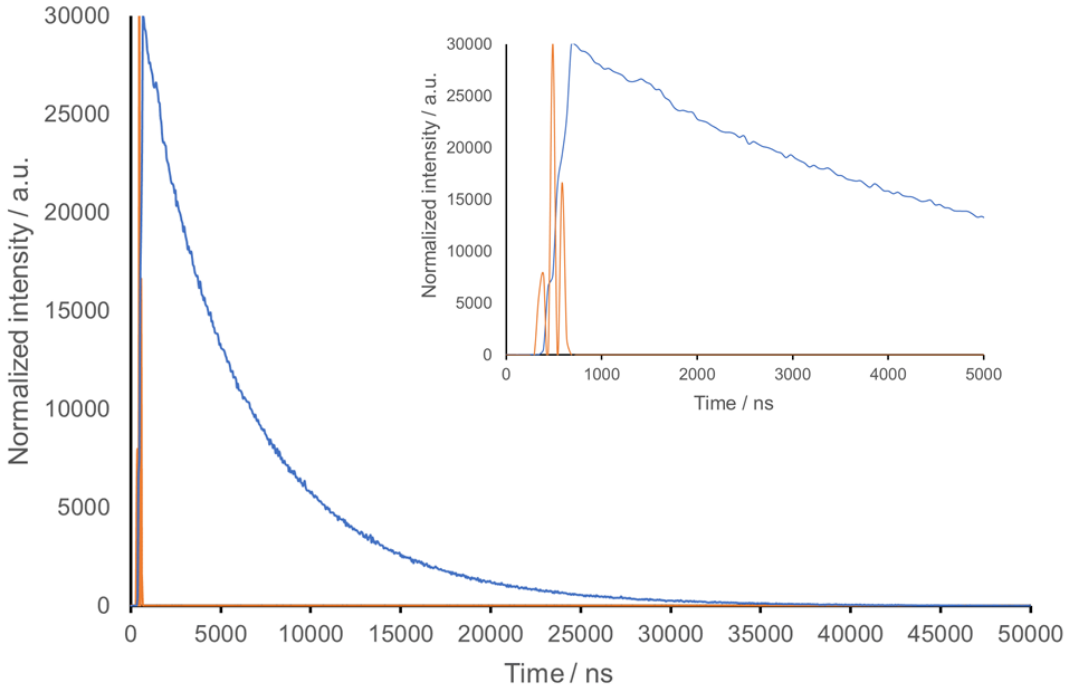


Figure S21. Solid-state lifetime decay of [Cu(POP)(**2**)][PF_6] (blue) and IRF (orange) (λ_{exc} = 365 nm).

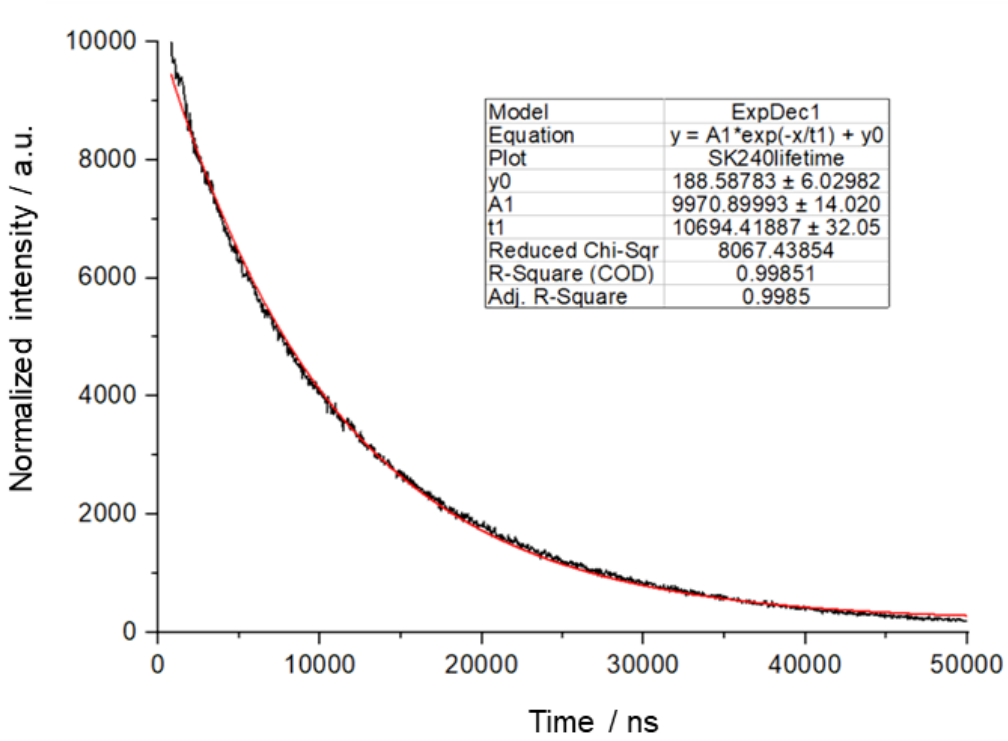


Figure S22. Solid-state lifetime decay (black) and first-order fitting curve (red) of [Cu(xantphos)(**2**)][PF_6] (λ_{exc} = 365 nm, exponential fitting done with Origin 2020).

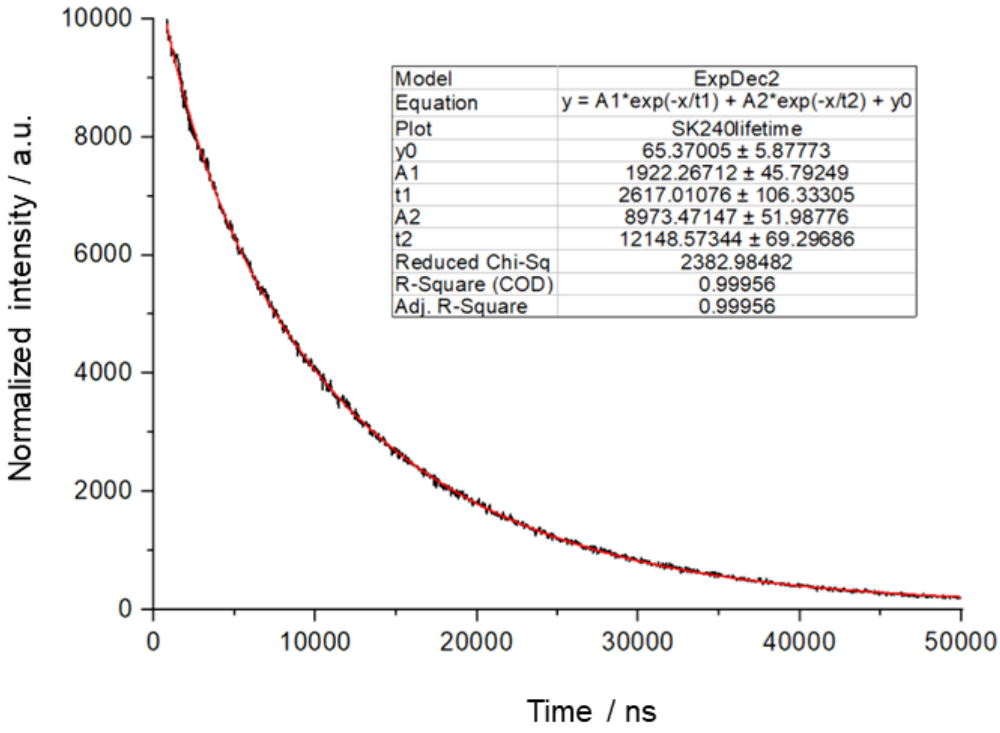


Figure S23. Solid-state lifetime decay (black) and second-order fitting curve (red) of [Cu(xantphos)(**2**)][PF_6] (λ_{exc} = 365 nm, exponential fitting done with Origin 2020).

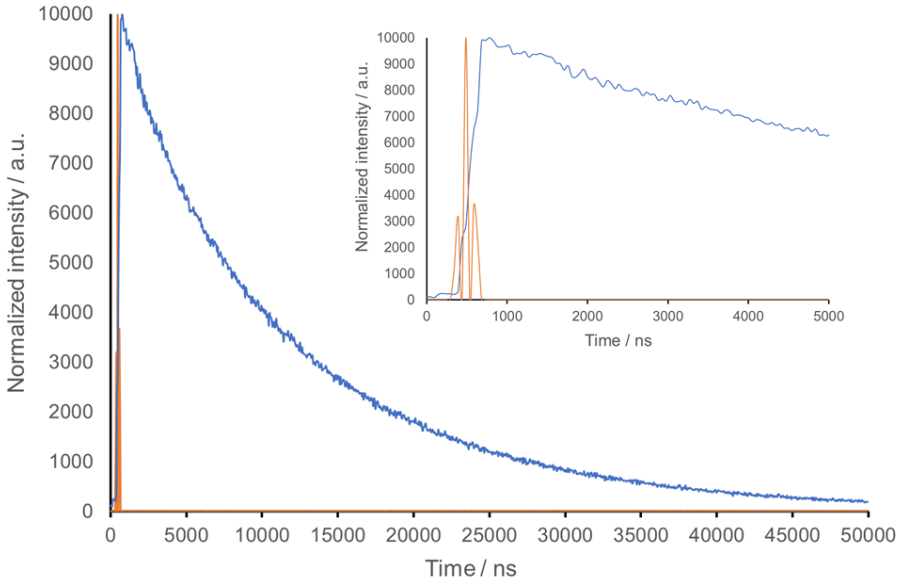


Figure S24. Solid-state lifetime decay of [Cu(xantphos)(**2**)][PF_6] (blue) and IRF (orange) (λ_{exc} = 365 nm).

Table S1. data including CSD refcodes for compounds included in Figure 12. .

CSD Refcode	Cu...O / Å	P^P ligand	Counterion
VICQOQ	2.947	POP	$[PF_6]^-$
UDOWUI	2.977	POP	$[PF_6]^-$

GABLAZ	3.012	POP	$[PF_6]^-$
VAWDOP	3.012	POP	$[PF_6]^-$
UDOVOB	3.046	POP	$[PF_6]^-$
VICROR	3.046	POP	$[PF_6]^-$
VAWDEF	3.048	POP	$[PF_6]^-$
MEWXOE	3.062	POP	$[PF_6]^-$
VICRIL	3.072	POP	$[PF_6]^-$
VAWFAD	3.093	POP	$[PF_6]^-$
UGANUO	3.096	POP	$[PF_6]^-$
UDOVUH	3.1	POP	$[PF_6]^-$
UDOXAP	3.118	POP	$[PF_6]^-$
UDOWES	3.129	POP	$[PF_6]^-$
MEWZIA	3.149	POP	$[PF_6]^-$
UDOXET	3.176	POP	$[PF_6]^-$
COYHEF	3.188	POP	$[BF_4]^-$
BOSVAI	3.199	POP	$[PF_6]^-$
MEWYEV	3.242	POP	$[PF_6]^-$
BOSYUF	3.247	POP	$[PF_6]^-$
GABVEN	3.253	POP	$[PF_6]^-$
EVAFAK	3.281	POP	$[PF_6]^-$
YITSIG	3.219	^{t}Bu$_2$xantphos[a]	$[PF_6]^-$
HIJRAW	3.244	^{t}Bu$_2$xantphos[a]	$[PF_6]^-$
VAWDUV	3.051	xantphos	$[PF_6]^-$
VICRAD	3.076	xantphos	$[PF_6]^-$
VANZES	3.083	xantphos	$[BF_4]^-$
VICREH	3.117	xantphos	$[PF_6]^-$
VANZAO	3.12	xantphos	$[BF_4]^-$
EVAFOY	3.121	xantphos	$[PF_6]^-$
GABMEE	3.124	xantphos	$[PF_6]^-$
VAWDIJ	3.148	xantphos	$[PF_6]^-$
EVAFEO	3.159	xantphos	$[PF_6]^-$
VANYUH	3.168	xantphos	$[BF_4]^-$
GABVAJ	3.175	xantphos	$[PF_6]^-$
VANYOB	3.198	xantphos	$[BF_4]^-$
EVADOW	3.203	xantphos	$[PF_6]^-$
MEWXUK	3.223	xantphos	$[PF_6]^-$
EVADUC	3.224	xantphos	$[PF_6]^-$
UDOWIW	3.225	xantphos	$[PF_6]^-$
UDOWAO	3.226	xantphos	$[PF_6]^-$
VICQUW	3.229	xantphos	$[PF_6]^-$
GABTUB	3.232	xantphos	$[PF_6]^-$
UDOXIX	3.234	xantphos	$[PF_6]^-$
GABWAK	3.244	xantphos	$[PF_6]^-$
MEWZAS	3.244	xantphos	$[PF_6]^-$
UDOXUJ	3.248	xantphos	$[PF_6]^-$
UDOWOC	3.25	xantphos	$[PF_6]^-$
UDOXOD	3.257	xantphos	$[PF_6]^-$
HIJQUP	3.081	xantphosMes$_2$[b]	$[PF_6]^-$
YITSOM	3.132	xantphosMes$_2$[b]	$[PF_6]^-$
VICQOQ	2.947	POP	$[PF_6]^-$

UDOWUI	2.977	POP	$[PF_6]^-$
GABLAZ	3.012	POP	$[PF_6]^-$
VAWDOP	3.012	POP	$[PF_6]^-$

[a] $^tBu_2$xantphos = 2,7-bis(*tert*-butyl)-4,5-bis(diphenylphosphino)-9,9-dimethylxanthene; [b] xantphosMes_2 = 4,5-bis(mesitylphenylphosphino)-9,9-dimethylxanthene.