Supporting Information:

A novel ruthenium(II) complex for two-photon absorption-based optical power limiting in the near-IR range.

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Table S3 Results of the TDDFRT calculations performed at the PBE0/DZVP2 level for the PTFF model at its optimised C₁ geometry; excitation energies (E, in cm⁻¹), corresponding wavelengths (λ, in nm), oscillator strengths (f), and assignments based on the molecular orbital (MO) diagram shown Figure S3.

Table S4 Results of the TDDFRT calculations performed at the PBE0/DZVP2 level for the PTFTF model at its optimised Cₛ geometry; excitation energies (E, in cm⁻¹), corresponding wavelengths (λ, in nm), oscillator strengths (f), and assignments based on the molecular orbital (MO) diagram shown Figure S4.
S1 - Ligands PF, PFF, PTFF and PTFTF

Figure S1: Molecular structure of the PF, PTF, PFF, PTFF, and PTFTF ligands
Figure S2. (a) Absorption spectra in CHCl₃, (b) Normalized excitation spectra in CH₂Cl₂, and (c) Normalized emission spectra in CH₂Cl₂ of the PF, PTF, PFF, PTFF, and PTFTF ligands.
**S2 - Theoretical characterisation of the ligands PFF, PTFF and PTFTF**

The ligands **PFF**, **PTFF** and **PTFTF** have been characterised theoretically using the models, which are shown in Figure S1, and which have been obtained by replacing the n-hexyl chains of the originals by hydrogen atoms. Density functional theory (DFT)\(^1\) has thus been applied to the determination of the Onsager cavity radii of these models, and their lowest-lying excited singlet states have been characterised by electronic excitation calculations performed within time-dependent density-functional response theory (TDDFRT).\(^2\)

![Models](image)

**Figure S3** Models used for the ligands **PFF**, **PTFF** and **PTFTF** and definitions of the angle $\phi$, which gives a measure of the angle between the average planes of the **P** and the closest **F** moiety, and of the angle $\psi$, which gives a measure of the angle between the average plane of the **F** moieties.

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**S2.1 Computational details**

The DFT and TDDFRT calculations were performed with the NWChem program package\(^3\) using the PBE0 hybrid functional\(^4\) and, for the description of all atoms, the Gaussian-type orbital (GTO) DFT basis set “DZVP2”\(^5\) of double-\(\zeta\) polarised quality. The geometries of the models have been optimised in their \(S_0\) ground state with no symmetry constraint, except for the PTFTF model whose symmetry was constrained to \(C_s\). Vibrational analyses performed on the calculated geometries led to real frequencies, indicating that these geometries correspond to true minima. The charge densities of the models have been calculated at the optimised geometries and used to estimate their Onsager cavity radii according to the formula

\[
a = \frac{3V_M}{4\pi^{1/3}} \quad 0.5 \text{ Å},
\]

where \(V_M\) is the molecular volume defined as the volume enclosed by the 0.001 au isodensity surface.\(^6\)

The TDDFT calculations were carried out with the Tamm-Dancoff approximation.\(^7\) Molecular visualization and the calculation of the molecular volumes were done with the Jmol program.\(^8\)

**S2.2 Results**

**S1.2.1 Optimised geometries and estimates of the Onsager radii**

For each ligand, there actually exist several rotamers, which differ by the values of the angles \(\phi\) and \(\psi\) ((\(\phi,\psi\)) in \([0,\pi]\)). Thus, if one rotamer is characterised by the couple of angles \((\phi_0,\psi_0)\), the other rotamers will be characterised by angles values close to \((\phi_0,\pi-\psi_0)\), \((\pi-\phi_0,\psi_0)\), and \((\pi-\phi_0,\pi-\psi_0)\). For the


present study, the calculations have been limited for each ligand to the characterisation of only one of its rotamers because the rotamers are expected to have very similar physico-chemical properties. Table 1000 summarises the \((\varphi,\psi)\) values found in the optimised geometries of the models as well as their calculated Onsager cavity radii.

The skeleton of the PFF model is not planar because of the steric interactions between neighbour H atoms pertaining to the P and the nearest F fragment \((\varphi > 0)\) and because of similar interactions involving H atoms pertaining to the two F fragments \((\psi > 0)\). On going to the PTFF model, the steric repulsion between the P and the nearest F fragment vanish, thanks to the insertion of the acetynyl (T) fragment. This translates into the planarity of the skeleton of the PTF moiety \((\varphi \sim 0)\), which is favourable to the delocalisation of the electronic \(\pi\) cloud over the whole PTF moiety. The insertion of T between the two F fragments is expected to similarly lead to a planar FTF skeleton. This is the reason as to why the calculations on the PTFTF model has been done with the symmetry constrained to \(C_s\) \((\varphi = \psi = 0)\). One also notes in Table 1000 that the predicted Onsager cavity radii slightly increase within the series, by 0.1 Å on going from the PFF to the PTFF model and also by 0.1 Å on going from the PTFF to the PTFTF model.

**Table S1** Theoretical characterisation of the models of the ligands in their S\(_0\) ground state :\((\varphi,\psi)\) values found in the optimised geometries of the models and values of the Onsager cavity radius

<table>
<thead>
<tr>
<th></th>
<th>PFF</th>
<th>PTFF</th>
<th>PTFTF</th>
</tr>
</thead>
<tbody>
<tr>
<td>((\varphi,\psi)) (in deg)</td>
<td>(123.1, 36.5)</td>
<td>(0.1, 35.5)</td>
<td>(0.0,0,0)(^a)</td>
</tr>
<tr>
<td>(a) (Å)</td>
<td>5.8</td>
<td>5.9</td>
<td>6.0</td>
</tr>
</tbody>
</table>

\(^a\) The \(C_s\) symmetry used in the calculations imposes \((\varphi, \psi) = (0.0,0,0)\).
S2.2.2 Lowest-lying $S_0 \rightarrow S_n$ electronic transitions ($n \leq 15$)

The features of the lowest-lying $S_0 \rightarrow S_n$ transitions of the PFF, PTFF and PTFTF models are summarised in Table S2, S3 and S4, respectively. These include the $S_0 \rightarrow S_n$ vertical excitation energies, the corresponding wavelengths, the associated oscillator strengths and the main characters of the transitions.

**Table S2** Results of the TDDFRT calculations performed at the PBE0/DZVP2 level for the PFF model at its optimised $C_1$ geometry: excitation energies (E, in cm$^{-1}$), corresponding wavelengths ($\lambda$, in nm), oscillator strengths ($f$), and assignments based on the molecular orbital (MO) diagram shown Figure S2.

<table>
<thead>
<tr>
<th>excited state</th>
<th>E</th>
<th>$\lambda$</th>
<th>$f$</th>
<th>major MO → MO transitions</th>
<th>main character</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$A</td>
<td>29461</td>
<td>339</td>
<td>1.59987</td>
<td>HOMO → LUMO (94%)</td>
<td>$\pi$[-FF] → $\pi$[PF-]</td>
</tr>
<tr>
<td>$^1$A</td>
<td>31310</td>
<td>319</td>
<td>0.00772</td>
<td>HOMO → LUMO+1 (75%)</td>
<td>$\pi$[-FF] → $\pi$[PF-]</td>
</tr>
<tr>
<td>$^1$A</td>
<td>32425</td>
<td>308</td>
<td>0.63478</td>
<td>HOMO → LUMO+2 (92%)</td>
<td>$\pi$[-FF] → $\pi$[PFF]</td>
</tr>
<tr>
<td>$^1$A</td>
<td>33240</td>
<td>301</td>
<td>0.00107</td>
<td>HOMO-3 → LUMO+1 (88%)</td>
<td>n[PF-] → $\pi$[PF-]</td>
</tr>
<tr>
<td>$^1$A</td>
<td>33381</td>
<td>300</td>
<td>0.00403</td>
<td>HOMO-3 → LUMO (65%)</td>
<td>n[PF-] → $\pi$[PF-]</td>
</tr>
<tr>
<td>$^1$A</td>
<td>34262</td>
<td>292</td>
<td>0.00601</td>
<td>HOMO-1 → LUMO+1 (31%)</td>
<td>$\pi$[PFF] → $\pi$[PF-]</td>
</tr>
<tr>
<td>$^1$A</td>
<td>34540</td>
<td>290</td>
<td>0.05687</td>
<td>HOMO-1 → LUMO (73%)</td>
<td>$\pi$[PF] → $\pi$[PF-]</td>
</tr>
<tr>
<td>$^1$A</td>
<td>35185</td>
<td>284</td>
<td>0.02921</td>
<td>HOMO → LUMO+4 (56%)</td>
<td>$\pi$[-FF] → $\pi$[-F-]</td>
</tr>
<tr>
<td>$^1$A</td>
<td>35815</td>
<td>279</td>
<td>0.00358</td>
<td>HOMO → LUMO+3 (32%)</td>
<td>$\pi$[-FF] → $\pi$[-FF]</td>
</tr>
<tr>
<td>$^1$A</td>
<td>36772</td>
<td>272</td>
<td>0.00580</td>
<td>HOMO-1 → LUMO+2 (45%)</td>
<td>$\pi$[PFF] → $\pi$[PFF]</td>
</tr>
<tr>
<td>$^1$A</td>
<td>36904</td>
<td>271</td>
<td>0.01316</td>
<td>HOMO-8 → LUMO (28%)</td>
<td>n$\pi$[PF-] → $\pi$[PF-]</td>
</tr>
<tr>
<td>$^1$A</td>
<td>37156</td>
<td>269</td>
<td>0.08024</td>
<td>HOMO-2 → LUMO (31%)</td>
<td>$\pi$[PF-] → $\pi$[PF-]</td>
</tr>
<tr>
<td>$^1$A</td>
<td>37371</td>
<td>268</td>
<td>0.00356</td>
<td>HOMO-8 → LUMO+1 (50%)</td>
<td>n$\pi$[PF-] → $\pi$[PF-]</td>
</tr>
<tr>
<td>$^1$A</td>
<td>37511</td>
<td>267</td>
<td>0.00265</td>
<td>HOMO-6 → LUMO (37%)</td>
<td>$\pi$[-F-] → $\pi$[PF-]</td>
</tr>
<tr>
<td>$^1$A</td>
<td>38306</td>
<td>261</td>
<td>0.00460</td>
<td>HOMO-5 → LUMO (35%)</td>
<td>n$\pi$[-F] → $\pi$[PF-]</td>
</tr>
</tbody>
</table>
Table S3 Results of the TDDFRT calculations performed at the PBE0/DZVP2 level for the PTFF model at its optimised C1 geometry: excitation energies (E, in cm⁻¹), corresponding wavelengths (λ, in nm), oscillator strengths (f), and assignments based on the molecular orbital (MO) diagram shown Figure S3.

<table>
<thead>
<tr>
<th>excited state</th>
<th>E</th>
<th>λ</th>
<th>f</th>
<th>major MO → MO transitions</th>
<th>main character</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>26280</td>
<td>381</td>
<td>2.35445</td>
<td>HOMO → LUMO (95%)</td>
<td>π[-TFF] → π[PTF-] CT</td>
</tr>
<tr>
<td>1A</td>
<td>29810</td>
<td>335</td>
<td>0.01206</td>
<td>HOMO → LUMO+1 (76%) HOMO-1 → LUMO+1 (13%)</td>
<td>π[-TFF] → π[P---] CT</td>
</tr>
<tr>
<td>1A</td>
<td>30772</td>
<td>320</td>
<td>0.51336</td>
<td>HOMO-1 → LUMO (55%) HOMO → LUMO+2 (39%)</td>
<td>π[PT-F] → π[PTF-] CT</td>
</tr>
<tr>
<td>1A</td>
<td>31690</td>
<td>316</td>
<td>0.10381</td>
<td>HOMO → LUMO+2 (49%) HOMO-1 → LUMO (36%)</td>
<td>π[-TFF] → π[P-FF] CT</td>
</tr>
<tr>
<td>1A</td>
<td>31916</td>
<td>313</td>
<td>0.00117</td>
<td>HOMO-3 → LUMO (82%) HOMO-3 → LUMO+2 (12%)</td>
<td>n[P---] → π[PTF-]</td>
</tr>
<tr>
<td>1A</td>
<td>33376</td>
<td>300</td>
<td>0.00003</td>
<td>HOMO-3 → LUMO+1 (89%)</td>
<td>n[P---] → π[P---]</td>
</tr>
<tr>
<td>1A</td>
<td>34013</td>
<td>294</td>
<td>0.00331</td>
<td>HOMO-1 → LUMO+1 (26%) HOMO-5 → LUMO (25%)</td>
<td>π[PT-F] → π[P---] + π[P---] → π[PTF-] CT</td>
</tr>
<tr>
<td>1A</td>
<td>34237</td>
<td>292</td>
<td>0.01528</td>
<td>HOMO → LUMO+4 (69%) HOMO-9 → LUMO (12%)</td>
<td>π[-TFF] → π[---F] CT</td>
</tr>
<tr>
<td>1A</td>
<td>35043</td>
<td>285</td>
<td>0.04036</td>
<td>HOMO-3 → LUMO+3 (36%) HOMO-2 → LUMO (23%)</td>
<td>π[-TFF] → π[---F] CT</td>
</tr>
<tr>
<td>1A</td>
<td>35597</td>
<td>281</td>
<td>0.09264</td>
<td>HOMO-1 → LUMO+2 (54%) HOMO → LUMO+3 (17%)</td>
<td>π[PT-F] → π[P-FF] CT</td>
</tr>
<tr>
<td>1A</td>
<td>35653</td>
<td>280</td>
<td>0.04496</td>
<td>HOMO → LUMO+5 (27%) HOMO-2 → LUMO (18%)</td>
<td>π[-TFF] → π[---F] CT</td>
</tr>
<tr>
<td>1A</td>
<td>35658</td>
<td>280</td>
<td>0.00994</td>
<td>HOMO-8 → LUMO (70%)</td>
<td>n[P---] → π[PTF-]</td>
</tr>
<tr>
<td>1A</td>
<td>36070</td>
<td>277</td>
<td>0.00977</td>
<td>HOMO-6 → LUMO (25%) HOMO-2 → LUMO (21%)</td>
<td>π[---F] → π[PTF-] CT</td>
</tr>
<tr>
<td>1A</td>
<td>36398</td>
<td>275</td>
<td>0.04129</td>
<td>HOMO-1 → LUMO+1 (23%) HOMO-5 → LUMO (23%)</td>
<td>π[PT-F] → π[---F] + π[P---] → π[PTF-] CT</td>
</tr>
<tr>
<td>1A</td>
<td>36918</td>
<td>271</td>
<td>0.17731</td>
<td>HOMO → LUMO+3 (21%) HOMO-5 → LUMO (12%)</td>
<td>π[-TFF] → π[---F] CT</td>
</tr>
</tbody>
</table>

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Table S4 Results of the TDDFRT calculations performed at the PBE0/DZVP2 level for the PTFTF model at its optimised \( C_s \) geometry: excitation energies (\( E \), in cm\(^{-1} \)), corresponding wavelengths (\( \lambda \), in nm), oscillator strengths (\( f \)), and assignments based on the molecular orbital (MO) diagram shown Figure S4.

<table>
<thead>
<tr>
<th>excited state</th>
<th>( E )</th>
<th>( \lambda )</th>
<th>( f )</th>
<th>major MO ( \rightarrow ) MO transitions</th>
<th>main character</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^1)A'</td>
<td>24967</td>
<td>401</td>
<td>2.99603</td>
<td>HOMO ( \rightarrow ) LUMO (95%)</td>
<td>( \pi[-\text{TFTF}] \rightarrow \pi[\text{PTF--}] ) CT</td>
</tr>
<tr>
<td>(^1)A'</td>
<td>29218</td>
<td>342</td>
<td>0.53509</td>
<td>HOMO ( \rightarrow ) LUMO+1 (61%)</td>
<td>( \pi[-\text{TFTF}] \rightarrow \pi[\text{P-FTF}] ) CT</td>
</tr>
<tr>
<td>(^1)A'</td>
<td>29701</td>
<td>337</td>
<td>0.01090</td>
<td>HOMO ( \rightarrow ) LUMO+2 (71%)</td>
<td>( \pi[-\text{TFTF}] \rightarrow \pi[\text{P---}] ) CT</td>
</tr>
<tr>
<td>(^1)A'</td>
<td>30616</td>
<td>327</td>
<td>0.05358</td>
<td>HOMO-1 ( \rightarrow ) LUMO+1 (30%)</td>
<td>( \pi[\text{PT-TF}] \rightarrow \pi[\text{PTF--}] ) CT</td>
</tr>
<tr>
<td>(^1)A''</td>
<td>31750</td>
<td>315</td>
<td>0.00110</td>
<td>HOMO-3 ( \rightarrow ) LUMO (73%)</td>
<td>( \eta[\text{P---}] \rightarrow \pi[\text{PTF--}] ) CT</td>
</tr>
<tr>
<td>(^1)A'</td>
<td>33214</td>
<td>301</td>
<td>0.01298</td>
<td>HOMO-1 ( \rightarrow ) LUMO+2 (22%)</td>
<td>( \pi[\text{PT-TF}] \rightarrow \pi[\text{P----}] ) CT</td>
</tr>
<tr>
<td>(^1)A''</td>
<td>33339</td>
<td>300</td>
<td>0.00002</td>
<td>HOMO-3 ( \rightarrow ) LUMO+2 (89%)</td>
<td>( \eta[\text{P----}] \rightarrow \pi[\text{P----}] ) CT</td>
</tr>
<tr>
<td>(^1)A'</td>
<td>33426</td>
<td>299</td>
<td>0.00984</td>
<td>HOMO ( \rightarrow ) LUMO+3 (33%)</td>
<td>( \pi[-\text{TFTF}] \rightarrow \pi[\text{P-F-F}] ) CT</td>
</tr>
<tr>
<td>(^1)A'</td>
<td>33810</td>
<td>296</td>
<td>0.17564</td>
<td>HOMO-1 ( \rightarrow ) LUMO+1 (65%)</td>
<td>( \pi[\text{PT-TF}] \rightarrow \pi[\text{P-FTF}] ) CT</td>
</tr>
<tr>
<td>(^1)A'</td>
<td>34085</td>
<td>293</td>
<td>0.03998</td>
<td>HOMO ( \rightarrow ) LUMO+4 (38%)</td>
<td>( \pi[-\text{TFTF}] \rightarrow \pi[-\text{F---}] ) CT</td>
</tr>
<tr>
<td>(^1)A'</td>
<td>34958</td>
<td>286</td>
<td>0.00099</td>
<td>HOMO ( \rightarrow ) LUMO+5 (47%)</td>
<td>( \pi[-\text{TFTF}] \rightarrow \pi[-\text{P---}] ) CT</td>
</tr>
<tr>
<td>(^1)A'</td>
<td>35520</td>
<td>282</td>
<td>0.00765</td>
<td>HOMO-6 ( \rightarrow ) LUMO (38%)</td>
<td>( \pi[-\text{F---}] \rightarrow \pi[\text{PTF--}] ) CT</td>
</tr>
<tr>
<td>(^1)A''</td>
<td>35558</td>
<td>281</td>
<td>0.00028</td>
<td>HOMO-8 ( \rightarrow ) LUMO (63%)</td>
<td>( \eta[\text{P----}] \rightarrow \pi[\text{PTF--}] ) CT</td>
</tr>
<tr>
<td>(^1)A'</td>
<td>35712</td>
<td>280</td>
<td>0.02549</td>
<td>HOMO-6 ( \rightarrow ) LUMO (20%)</td>
<td>( \pi[-\text{F---}] \rightarrow \pi[\text{PTF--}] ) CT</td>
</tr>
<tr>
<td>(^1)A'</td>
<td>36132</td>
<td>277</td>
<td>0.16715</td>
<td>HOMO-4 ( \rightarrow ) LUMO (21%)</td>
<td>( \pi[-\text{F---}] \rightarrow \pi[\text{PTF--}] ) CT</td>
</tr>
</tbody>
</table>
**Figure S4** Diagram of the frontier Kohn-Sham molecular orbitals determined at the PBE0/DZVP2 level for the PFF model at its optimised $C_i$ geometry.
Figure S5 Diagram of the frontier Kohn-Sham molecular orbitals determined at the PBE0/DZVP2 level for the PTFF model at its optimised $C_1$ geometry.
Figure S6 Diagram of the frontier Kohn-Sham molecular orbitals determined at the PBE0/DZVP2 level for the PTFTF model at its optimised $C_s$ geometry (the symmetries of the orbitals, $a'$ or $a''$, are indicated).