A theoretical investigation on two-photon absorption and fluorescent properties of coumarin-based derivatives for Pd²⁺ detection

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Supporting Information

A. Table of contents

- 1. Table S1. The one-photon absorption and fluorescence emission spectra calculated by different functionals in PCM for P'1 and P'5.
- Table S2. The calculated results of OPA and fluorescence spectra of synthesized P'1 and P'5 by using different basis set.
- Table S3. The calculated results of smallest three vibrational frequency values for all studied molecules in ground state by two functionals.
- Figure S1. Chemical structures of the all Pd²⁺ probes studied in this work (blue groups are the modified parts).
- Figure S2. Optimized ground state geometries of the studied Pd²⁺ probe molecules calculating at M06-2X* (44% HF)/6-31+G(d) level with explicit and implicit water solvent model.
- Figure S3. Optimized ground state geometries of the studied product molecules according to M06-2X* (44% HF)/6-31+G(d) method with explicit and implicit water solvent model.
- Figure S4. Electron density plots of HOMO and LUMO for all molecules by using M06-2X* (44%HF) /6-31+G(d) method with explicit and implicit water solvent model.
- 8. Figure S5. The atomic labels of –OCH₂CCH and –OH groups for R1 and P'1, respectively.
- Figure S6. Comparison of ground state and first-excited state geometries for R1 and P'1 (magentas for S₀ and green for S₁) by applying M06-2X* (44%HF) /6-31+G(d) method.
- 10. Figure S7. Simulated TPA spectra of P'1 by different functionals in DALTON program.
- 11. Table S4. TPA related parameters of Pd²⁺ probe molecules by DALTON program.
- B. The derivative calculated details of $S_1 \rightarrow T_1$ ISC rate (K_{ISC}).
- 1. Table S5. The calculated $\Delta E_{S_1 \to T_1}$ values of R1 and P'1 by different functionals.
- 2. Table S6. The calculated $|\langle S_1 | H_{S0} | T_1 \rangle| / cm^{-1}$ values of R1 and P'1 by different basis sets.

3. Table S7. Calculated effective spin-orbit coupling matrix elements $|\langle S_1 | H_{S0} | T_1 \rangle|$ in cm⁻¹) between S₁ and T₁ states at the optimized S₁ geometries by the TDDFT//M06-2X/6-31+G(d) method, the energy difference (${}^{\Delta E_{S_1} \rightarrow T_1}$ in eV) between the minima of S₁ and T₁, the rate of ISC process (K_{ISC} in S⁻¹) from S₁ to T₁.

	P'1				P'5			
Method	$\lambda_{max/nm}^{o}$	f^{o}	$\lambda_{max/nm}^{\ e}$	f^e	$\lambda_{max/nm}^{o}$	f^{o}	$\lambda_{max/nm}^{\ e}$	f^e
B3LYP	373.6	0.27	448.1	0.45	384.5	0.94	482.4	1.16
B3LYP-explicit	399.6	0.39	484.2	0.49	397.0	0.78	482.4	0.99
CamB3LYP-explicit	367.4	0.50	460.4	0.63	362.9	0.96	440.9	1.23
M06-explicit	392.8	0.42	473.2	0.53	389.5	0.84	485.4	1.07
BHandHLYP-explicit	353.2	0.54	434.7	0.67	358.3	0.98	481.8	1.18
PBE0-explicit	390.3	0.42	474.6	0.52	394.2	0.84	475.9	1.09
wB97XD-explicit	360.0	0.47	460.3	0.62	351.0	1.00	435.0	1.24
M06-2X-explicit	368.5	0.49	465.6	0.62	354.2	1.00	442.3	1.24
M06-2X*(HF=44%)-explicit	385.6	0.43	505.3	0.58	415.6	0.97	483.7	1.20
M06-2X*(HF=15%)-explicit	488.6	0.18	700.6	0.34	428.1	0.76	668.8	0.97
BLYP-explicit	452.4	0.20	573.1	0.23	465.9	0.11	599.6	0.36
Exp.	386		514		450		490	

Table S1. The one-photon absorption and fluorescence emission spectra calculated by different functionals in PCM for P'1 and P'5.

B3LYP denotes TDDFT//B3LYP/6-31+G(d) along with implicit water model; B3LYP-explicit stands for TDDFT//B3LYP/6-31+G(d) following with explicit and implicit water solvent model.

Table S2 The calculated results of OPA and fluorescence spectra of synthesized P'1 and	P'5 by
using different basis set.	

	P'1				P'5			
Basis	$\lambda_{max/nm}^{o}$	f^o	$\lambda_{max/nm}^{\ e}$	f ^e	$\lambda_{max/nm}^{o}$	f^o	$\lambda_{max/nm}^{\ e}$	f ^e
6-31G	379.6	0.41	470.3	0.56	364.4	0.95	461.4	1.16
6-31G (d)	381.5	0.42	487.8	0.56	370.0	0.96	471.3	1.21
6-31G (d, p)	381.9	0.42	488.6	0.56	370.4	0.96	471.8	1.27
6-31+G (d)	385.6	0.43	505.3	0.58	415.6	0.97	483.7	1.20
6-31++G (d)	390.7	0.43	506.1	0.58	415.9	0.94	483.8	1.20
Exp.	386		514		450		490	

Malaaulaa	M06-2X	*(HF=44%)/6	-31+G(d)	⁶⁰ B97XD/6-31+G(d)			
	Freq1 ^a /cm ⁻¹	Freq2 ^a /cm ⁻¹	Freq3 ^a /cm ⁻¹	Freq1/cm ⁻¹	Freq2/cm ⁻¹	Freq3/cm ⁻¹	
R1	56.01	66.38	71.48	58.42	72.50	74.05	
P'1	61.70	70.19	78.09	65.77	74.29	82.51	
R2	50.15	72.09	81.83	51.06	74.91	79.87	
P'2	54.75	74.21	82.14	55.45	80.46	88.99	
R3	52.00	63.30	66.40	53.76	64.75	67.09	
P'3	61.83	67.87	75.70	62.15	70.05	80.03	
R4	53.25	62.95	69.12	53.57	63.62	69.28	
P'4	62.67	69.91	72.60	65.41	71.77	74.38	
R5	49.24	53.14	72.14	52.97	55.53	73.01	
P'5	51.32	56.06	69.94	53.49	57.57	72.43	
R6	48.33	60.40	69.64	53.37	66.39	69.55	
P'6	53.69	63.70	74.36	58.50	70.34	76.74	
R7	48.05	63.09	66.12	52.98	64.89	66.86	
P'7	52.01	62.78	74.07	54.86	66.32	74.47	
R8	46.26	58.97	64.62	52.09	63.81	65.28	
P'8	50.35	61.81	72.46	56.08	67.60	76.54	
R 9	46.32	59.88	62.17	48.02	62.17	63.88	
P'9	48.55	62.66	73.71	51.23	63.39	75.32	

Table S3 The calculated results of smallest three vibrational frequency values for all studied molecules in ground state by two functionals.

a: Freq1, Freq2, Freq3 are the smallest three vibrational frequency values of every molecule including explicit water molecules.



Figure S1. Chemical structures of the all Pd²⁺ probes studied in this work (blue groups are the modified parts).



Figure S2. Optimized ground state geometries of the studied Pd^{2+} probe molecules calculating at M06-2X* (44% HF)/6-31+G(d) level with explicit and implicit water solvent model.



Figure S3. Optimized ground state geometries of the studied product molecules according to M06-2X* (44% HF)/6-31+G(d) method with explicit and implicit water solvent model.



Figure S4. Electron density plots of HOMO and LUMO for all molecules by using M06-2X* (44%HF)/6-31+G(d) method with explicit and implicit water solvent model.



Figure S5. The atomic labels of -OCH₂CCH and -OH groups for R1 and P'1, respectively.



Figure S6. Comparison of ground state and first-excited state geometries for R1 and P'1 (magentas for S_0 and green for S_1) by applying M06-2X* (44%HF) /6-31+G(d) method.



Figure S7. Simulated TPA spectra of P'1 by different functionals in DALTON program.

Mol.	$\lambda_{max/nm}^{T}$	$\delta_{max/GM}^{T}$	Transition Character	σ	Mol.	$\lambda_{max/nm}^{T}$	$\delta_{max/GM}^{T}$	Transition Character	σ
R1	861.1	100.61	$S_0 \rightarrow S_1$	0.40	R5	867.1	17.21	$S_0 \rightarrow S_1$	0.05
R2	797.4	51.63	$S_0 \rightarrow S_1$	0.19	R6	864.1	46.92	$S_0 \rightarrow S_1$	0.16
R3	880.7	111.57	$S_0 \rightarrow S_1$	0.32	R 7	846.4	68.41	$S_0 \rightarrow S_1$	0.20

R4	965.0	118.26	$S_0 \rightarrow S_1$	0.42	R8	1042.0	151.00	$S_0 \rightarrow S_1$	0.46
					R8	992.0	277.47	$S_0 \rightarrow S_1$	0.74

B. The derivative calculated details of $S_1 \rightarrow T_1$ ISC rate (K_{ISC}).

Here, we calculated the intersystem crossing rate K_{ISC} . To our knowledge, within the framework of time-dependent first-order perturbation theory and under the Condon approximation, the rate constant $K_{i \rightarrow f}$ of $S_1 \rightarrow T_1$ ISC (intersystem crossing rate K_{ISC}) is given by the well-known Fermi golden rule expression:[1,2]

$$k_{i \to f}^{0} = \frac{2\pi}{\hbar} |H_{SO}|^2 \sum_{\nu} \sum_{\nu} P_{i\nu} |\langle \Theta_{f\nu} | \Theta_{i\nu} \rangle|^2 \delta \left(\Delta E_{if} + E_{\nu}^{i} - E_{\nu}^{f} \right)$$

Here. $|H_{SO}| = \langle \Phi_f | H_{SO} | \Phi_i \rangle$ is spin-orbit coupling (SOC) matrix element between the initial and final electronic state. P_{iv} represents the Boltzmann distribution function of the initial-state vibronic manifold at finite temperature; $\langle \Theta_{f\nu} | \Theta_{i\nu} \rangle$ denotes the overlap between the vibrational wave functions; the delta function can be Fourier transformed as $\delta\left(\Delta E_{if} + E_{\nu}^{i} - E_{\nu}^{f}\right) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} d\tau e^{i\Delta E_{if}\tau} e^{i\left(E_{\nu}^{i} - E_{\nu}^{f}\right)\tau}$. It is knowledge that the $|H_{SO}|$ and ΔE_{if} (the difference between the energy minima of the initial and final electronic states) have important

influence on the $K_{i \rightarrow f}$ (K_{ISC}), value. The calculated $|H_{SO}|$, ΔE_{if} and K_{ISC} of R1, P'1, R4, P'4 and P'5 are listed in Table S7.

Here, some popular functionals with different Hartree-Fock (HF) exchange percentage, e.g. M062X (44%HF), PBE0 (25%HF), B3LYP (20%HF), BLYP (0%HF) were tested for $\Delta E_{S_1 \rightarrow T_1}$ of the synthesized R1 and P'1 to verify the deviation resulting from the functional. As displayed in Table S5, the $\Delta E_{S_1 \rightarrow T_1}$ value deviation of synthesized R1 and P'1 calculating by different functionals could be negligible. Moreover, not only probe R1 but also product P'1, its $\Delta E_{S_1 \rightarrow T_1}$ value is very large compared with these compounds following intersystem crossing nature.[3] Such large energy gap $\Delta E_{S_1 \rightarrow T_1}$ demonstrates that it is almost impossible to happen intersystem crossing process in the excited state. Additionally, effective spin-orbit coupling (SOC) matrix elements ($|\langle S_1 | H_{S0} | T_1 \rangle|/cm^{-1}$) between S₁ and T₁ are calculated by using TDDFT method

implemented in the Beijing Density Functional (BDF) program.[4,5] TDDFT methods have been employed to calculate SOC matrix elements in many studies.[6,7] Similarly, in order to consider the basis sets influence on the $|\langle S_1 | H_{SO} | T_1 \rangle|$, we calculated the $|\langle S_1 | H_{SO} | T_1 \rangle|$ values for the synthesized R1 and P'1 by different functionals and basis sets displayed in Table S6. From Table S6, it can be found that the effective SOC matrix elements in these pure organic molecules are extremely small (< 1 cm⁻¹) with different simulation level.

At last, the K_{ISC} are obtained by performing MOMAP software which has been successfully used in the organic molecules properties explanations.[8-10] The energy difference $\Delta E_{S_1 \rightarrow T_1}$, $|\langle S_1 | H_{SO} | T_1 \rangle|$ and K_{ISC} between the minima of S₁ and T₁ for R1, P'1 R4, P'4 and P'5 all calculated at the TDDFT//M06-2X/6-31+G* level. The calculated results are listed in Table S7. From Table S7, we can see that the $\Delta E_{S_1 \rightarrow T_1}$ values are large enough to inhibit the ISC process. Furthermore, the small effective SOC matrix elements (below 1 cm⁻¹) reduce the K_{ISC} value significantly. The K_{ISC} value is much smaller than the corresponding K_{IC}. Thus the ISC process could be negligible in this study although some reported coumarin derivatives possessing phosphorescence properties at very low temperature (77K).[11,12] Here, these studied two-photon fluorescent molecules are used in room temperature (300K), and the fluorescent optical signals were confirmed from experiments.[13,14]

Table S5 The calculated $\Delta E_{S_1 \rightarrow T_1}$ values of R1 and P'1 by different functionals.

	M062x	PBE0	B3LYP	BLYP
R1	0.87 eV	1.09 eV	0.82 eV	0.81 eV
P'1	0.88 eV	1.10 eV	0.84 eV	0.82 eV

Table S6 The calculated $|\langle S_1 | H_{S0} | T_1 \rangle| / cm^{-1}$ values of R1 and P'1 by different basis sets.

	R1/cm ⁻¹	P'1/cm ⁻¹
M06-2X/6-31+G*	0.07	0.03
M06-2X/6-31G*	0.01	0.01
M06-2X/6-31++G*	0.18	0.06
M06-2X/cc-PVTZ	0.01	0.01

Table S7 Calculated effective spin-orbit coupling matrix elements $|\langle S_1 | H_{S0} | T_1 \rangle|$ in cm⁻¹) between S1 and T1 states at the optimized S1 geometries by the TDDFT//M06-2X/6-31+G(d) method, the energy difference (${}^{\Delta E_{S_1} \rightarrow T_1}$ in eV) between the minima of S₁ and T₁, the rate of ISC process (K_{ISC} in S⁻¹) from S₁ to T₁.

	R1	P'1	R4	P'4	P'5
$ \langle S1 H_{S0} T1 \rangle /_{\mathrm{cm}^{-1}}$	0.07	0.03	0.39	0.52	0.09
$\Delta E_{S_1 \to T_1/eV}$	0.87	0.88	1.08	0.94	0.73
K _{ISC}	6.44×10 ³	8.16×10 ²	5.24×10 ³	1.44×10 ²	2.56×10 ²

Additionally, thermally activated decay via triplet state *i.e.* TADF process could accelerate the non-radiative decay. But it is known that metal-free organic aromatic compounds with TADF nature usually have the following characters: (i) the energy gaps $\Delta E_{S_1 \rightarrow T_1}$ is very small (< 0.1 eV); (ii) there are internal rotations around the single bond between donor (D) and acceptor (A) in molecular fragments, for example butterfly-shaped D–A–D chromophores; (iii) the HOMOs is degenerated to giving rise to the electron configurations with the same energies for these low-lying excited states.[2] Of particular note that: (1) the energy gaps $\Delta E_{S_1 \rightarrow T_1}$ of the studied coumarin derivatives are large enough (> 0.80 eV) to restrict the ISC and RISC; (2) the geometries of all the studied coumarin derivatives don't possess the internal rotational single bond between donor and acceptor evidently; (3) according to the electronic structural properties shown in Figure 3, no degenerated HOMOs are found in all the studied molecules. Eventually, these suggested that there is not thermally activated decay via triplet state in the studied chromophores. Internal conversion from vibration should be related to the nonradiative decay for the fluorescence chromophores, although the measured K_{IC} values are not been reported in the experimental results.[13,14]

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