Supporting Information

The Distinct O₂ Quenching Mechanism between Fluorescence and Phosphorescence for Dyes Adsorbed on the Silica Gel

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Experimental Section

General comments

4-bromo-(N,N-diphenyl)-aniline,¹ 4-bromo-4'-(N,N-diphenylamino)-biphenyl, 4bromo-4''-(N,N-diphenylamino)-terphenyl,² 4-(N,N-diphenylamino)-benzeneboronic acid,1 4-ethynyl-N,N-diphenylaniline,³ 4-(N,N-diphenylamino)biphenyl-4'-boronic acid,² 10-bromo-9-(N,N-diphenylamino)-anthracene,⁴ (4-(N,Ndiphenylamino)phenyl)diphenylphosphine⁵ were synthesized according to the published procedures. Tetrahydrofuran (THF), toluene and diethyl ether were distilled over Na-benzophenone ketyl under a nitrogen atmosphere prior to use. Other reagents and solvents were used as received from suppliers. The solution ${}^{1}H$, ${}^{31}P{}^{1}H$, ${}^{13}C{}^{1}H$ and ¹H–¹H COSY NMR spectra were recorded on Bruker Avance 400 and AMX-400 spectrometers. Mass spectra were recorded on a Bruker maXis II ESI-QTOF instrument in the ESI⁺ mode. Microanalyses were carried out at the analytical laboratory of the University of Eastern Finland. The silica gel materials (porous size of 6 nm in diameter) used in this study was purchased from Merck, and the other (porous size of 12, 20, 30, and 100 nm in diameter) were purchased from YMC. Samples were prepared by dissolved in dichloromethane and then dropped on the silica gel. All samples deposited on the silica gel were dried at 60 °C for one hour to remove the residual solvent.

Photophysical measurements

Samples after preparation were measured using an Edinburgh (FS920) fluorimeter, equipped with a Linkam THMS 600 hot stage (Linkam Scientific Instruments, United Kingdom). Lifetimes were determined by the Time-Correlated Single Photon Counting (TCSPC) method, using Edinburgh FL 900 photon-counting system with a hydrogen-filled lamp as the excitation source (Edinburgh Instruments, UK). The population decays were fitted using Edinburg Instruments software by nonlinear least square fitting method with the deconvolution of instrument response function. Oxygen concentration was adjusted using gas dilution system DS-02 (Peak technology, Taiwan) equipped with mass flow controller EL-FLOW Base (Bronkhorst, Netherlands, 1500 sccm) with nitrogen as the dilution gas to probe fluorescence intensity and relaxation dynamics as a function of O₂ concentration. The gas system was connected to thermostatic cuvette holder GS21530 (Specac, UK) with temperature controller Eurotherm 2216e (Specac, UK) so that temperature-dependent measurements could be performed.

Synthesis

4-Bromo-1-(*N***,***N***-diphenylamino)-naphthalene**. The synthesis was carried out under a nitrogen atmosphere. A mixture of compounds 1,4-dibromonaphthalene (3.00 g, 10.40 mmol), *N*,*N*-diphenylamine (1.80 g, 10.40 mmol), sodium t-butoxide (1.00 g, 10.40

mmol), Pd(OAc)₂ (0.24 g, 0.4 mmol) and tris(o-tolyl)phosphine (0.36 g, 1.2 mmol) in toluene (80 ml) was stirred at 90 °C for 48 h. After cooling down to room temperature, the reaction mixture was poured in water (150 mL), washed with brine (2 x 100 mL) and extracted with dichloromethane (3 x 50 mL). Combined organic layers were dried over anhydrous Na₂SO₄, filtered through Celite and evaporated *in vacuo*. The resulting brown oil was purified by column chromatography (Silica gel 70-230 mesh, 4 × 20 cm, eluent dichloromethane-hexane, 1:5 v/v) and further recrystallized from hot hexane to afford green-yellow crystals (1.0 g, 33 %). ¹H NMR (CDCl₃, 298 K; δ): 8.28 (d, *J*_{HH} = 8.5 Hz, -naphthalene-, 1H), 7.99 (d, *J*_{HH} = 8.5 Hz, -naphthalene-, 1 H), 7.78 (d, *J*_{HH} = 8.0 Hz, -naphthalene-, 1H), 7.58 (ddd, *J*_{HH} = 8.3, 6.9, 1.1 Hz, -naphthalene-, 1H), 7.42 (ddd, *J*_{HH} = 8.0, 6.9, 1.1 Hz, -naphthalene-, 1H), 7.18–7.27 (m, -naphthalene- and meta-H NPh2, 5H), 7.03 (d, *J*_{HH} = 9.7 Hz, ortho-H NPh2, 4H), 6.97 (t, *J*_{HH} = 6.8 Hz, para-H NPh2, 2H).

General procedure for the preparation of compound 1-3

N,N-diphenylamino-bromoaryl (1.00 eq.), NiBr₂ (0.20 eq.), triphenylphosphine (1.05 eq.) and ethylene glycol (3 mL) were placed in a 15 mL sealed tube. The suspension was degassed by purging nitrogen for 20 min, and stirred for 5 hours at 180–190 °C. Then the reaction mixture was cooled down to room temperature and poured into dichloromethane (50 mL). The organic layer was washed with water (2 × 100 mL), dried over anhydrous Na₂SO₄, filtered through a pad of Celite and evaporated *in vacuo*. The residue was purified by column chromatography (Silica gel 70-230 mesh, \emptyset 3×20 cm, eluent dichloromethane-methanol, 99:1→92:8 v/v mixture) to afford phosphonium salts **1–3** as amorphous solids.

(4-(*N*,*N*-diphenylamino)phenyl)triphenylphosphonium bromide (1).

Prepared from 4-bromo-(*N*,*N*-diphenyl)-aniline (0.50 g, 1.54 mmol), NiBr₂ (0.07 g, 0.31 mmol), triphenylphosphine (0.42 g, 1.62 mmol) at 180 °C to afford white solid (0.83 g, 92 %). ESI-MS (*m/z*): [M]⁺ 506.2060 (calcd 506.2038). ¹H NMR (CD₂Cl₂, 298 K; δ): 7.91–7.95 (m, *para*-H PPh₃⁺, 3H), 7.78 (td, *J*_{HH} = 7.9, 3.5 Hz, *meta*-H PPh₃⁺, 6H), 7.63–7.69 (m, *ortho*-H PPh₃⁺, 6H), 7.43–7.47 (m, *meta*-H NPh₂, 4H), 7.28–7.33 (m, *ortho*-H NPh₂ and -ph-, 8H), 7.08–7.11 (m, *para*-H NPh₂, 2H). ¹³C{¹H} NMR (CD₂Cl₂; 298 K; δ): 144.8, 135.5 (d, *J* = 11.8 Hz), 135.3 (d, *J* = 3.0 Hz), 134.2 (d, *J* = 10.3 Hz), 130.4 (d, *J* = 12.8 Hz), 130.1, 126.9, 126.4, 119.3, 118.6, 118.4, 118.3. ³¹P{¹H} NMR (CD₂Cl₂; 298 K; δ): 22.0 (s, 1P, PPh₃⁺). Anal. Calcd for C₃₆H₂₉PNBr: C, 73.72; H, 4.98; N, 2.39. Found: C, 73.61; H, 5.20; N, 2.28.

(4'-(*N*,*N*-diphenylamino)biphenyl-4-yl)triphenylphosphonium bromide (2).

Prepared from 4-bromo-4'-(*N*,*N*-diphenylamino)-biphenyl (0.36 g, 0.91 mmol), NiBr₂ (0.04 g, 0.18 mmol), triphenylphosphine (0.25 g, 0.95 mmol) at 180 °C to afford

greenish solid (0.54 g, 89 %). ESI-MS (*m/z*): $[M]^+$ 582.2348 (calcd 582.2351). ¹H NMR (CDCl₃, 298 K; δ): 7.91–7.95 (m, *para*-H PPh₃⁺ and -biph-, 5H), 7.78 (td, *J*_{HH} = 7.9, 3.5 Hz, *meta*-H PPh₃⁺, 6H), 7.63–7.71 (m, *ortho*-H PPh₃⁺ and -biph-, 8H), 7.54 (d, *J*_{HH} = 8.6 Hz, -biph-, 2H), 7.30 (dd, *J*_{HH} = 7.7 Hz, *meta*-H NPh₂, 4H), 7.11–7.16 (m, *ortho*-H NPh₂ and -biph-, 6H), 7.09 (t, *J*_{HH} = 7.7 Hz, *para*-H NPh₂, 2H). ¹³C{¹H} NMR (CDCl₃; 298 K; δ): 149.9, 148.5, 147.6, 136.5, 135.6 (d, *J* = 11.4 Hz), 135.0 (d, *J* = 10.0 Hz), 131.6 (d, *J* = 12.8 Hz), 131.1, 130.1. 129.0, 128.8, 125.9, 124.5, 123.1, 118.4 (d, *J* = 89.5 Hz), 115.1. ³¹P{¹H} NMR (CD₂Cl₂; 298 K; δ): 23.5 (s, 1P, PPh₃⁺). Anal. Calcd for C₄₂H₃₃PNBr: C, 76.13; H, 5.02; N, 2.11. Found: C, 76.00; H, 5.23; N, 2.01.

(4-(*N*,*N*-diphenylamino)naphthalen-1-yl)triphenylphosphonium bromide (3).

Prepared from 4-bromo-1-(*N*,*N*-diphenylamino)-naphthalene (0.35 g, 0.94 mmol), NiBr₂ (0.04 g, 0.18 mmol), triphenylphosphine (0.26 g, 0.99 mmol) at 190 °C. Yellow precipitate (0.20 g, 34 %). ESI-MS (*m/z*): $[M]^{1+}$ 556.2186 (calcd 556.2194). ¹H NMR (CD₂Cl₂, 298 K; δ): 8.18 (d, *J*_{HH} = 8.6 Hz, -naphthalene-, 1H), 7.93 (td, *J*_{HH} = 8.3, 7.9, 2.0 Hz, *para*-H PPh₃⁺, 3H), 7.69–7.79 (m, *meta*+*ortho*-H PPh₃⁺, 12H), 7.32–7.48 (m, *meta*-H NPh₂ and -naphthalene-, 8H), 7.25 (dd, *J*_{HH} = 8.1, 2.5 Hz, -naphthalene-, 1H), 7.15 (t, *J*_{HH} = 7.4 Hz, *para*-H NPh₂, 2H), 7.15 (d, *J*_{HH} = 8.6 Hz, *ortho*-H NPh₂, 4H). ¹³C{¹H} NMR (CDCl₃; 298 K; δ): 148.8, 139.9 (d, *J*=11.8 Hz), 136.2, 134.9 (d, *J* = 10.6 Hz), 131.9 (d, *J* = 13.2 Hz), 130.4, 129.4, 127.9, 127.4, 125.1, 124.1, 123.9, 119.6, 118.7. ³¹P{¹H} NMR (CDCl₃; 298 K; δ): 22.6 (s, 1P, PPh₃⁺). Anal. Calcd for C₄₀H₃₁PNBr: C, 75.47; H, 4.91; N, 2.20. Found: C, 75.30; H, 5.08; N, 2.22.



Figure S1. The fluorescence intensity of compound 1 on the silica gel (porous size of 6 nm in diameter) as a function of O_2 concentration (in % of volume, see text) at room temperature and with excitation at $\lambda_{ex} = 350$ nm. The upper inset: The decay of fluorescence of compound 1 under 0% and 50% O_2 on the silica gel at room temperature. The lower inset: A plot of I_0/I for compound 1 on the silica gel at room temperature as a function of applied O_2 concentration.



Figure S2. The fluorescence intensity of compound **3** on the silica gel (porous size of 6 nm in diameter) as a function of O_2 concentration (in % of volume, see text) at room temperature and with excitation at $\lambda_{ex} = 350$ nm. The upper inset: The decay of fluorescence of compound **3** under 0% and 50% O_2 on the silica gel at room temperature. The lower inset: A plot of I₀/I for compound **3** on the silica gel at room temperature as a function of applied O_2 concentration.



Figure S3. The fluorescence intensity of compound 2 on the silica gel as a function of O₂ concentration (in % of volume, see text) from (a) 0% to 100%, and (b) 100% to 0% at room temperature and with excitation at $\lambda_{ex} = 350$ nm.



Figure S4. The fluorescence intensity of compound 2 on the silica gel with porous size of (a) 12 nm, (b) 20 nm, (c) 30 nm, and (d) 100 nm in diameter as a function of O₂ concentration (in % of volume, see text) at room temperature and with excitation at $\lambda_{ex} = 350$ nm.

Stern-Volmer equations

Standard Stern-Volmer equations in solution

The Stern-Volmer equations with in terms of dynamic and static quenching can be expressed in eq. (1) and (2), respectively.^{6, 7}

$$\frac{\tau_0}{\tau} = 1 + K_{SV}[Q] \tag{1}$$

$$\frac{I_0}{I} = 1 + (K_{SV} + K_{eq})[Q] + K_{SV}K_{eq}[Q]^2$$
(2)

where [Q] is the quencher concentration, τ 's are lifetimes, I's are emission intensities, K_{SV} is the Stern-Volmer constant, and K_{eq} is the association constant for binding of the quencher to the luminescent species. The subscript 0 denotes the value in the absence of quencher. If plots of τ_0/τ or I₀/I versus quencher concentration are linear and match, quenching is purely dynamic (i.e., Keq = 0). If τ_0/τ is above I₀/I, static quenching is present.

Applying standard Stern-Volmer equations to O_2 quenching phosphorescence on solid phase

The reason for nonlinear Stern-Volmer curves in solid phase (see in text) is preliminarily explained by involving both dynamic and static quenching, for which the low temperature facilitates the formation of nonphosphorescent complex between the adsorbed organic molecules and oxygen.⁸⁻¹⁰ In order to ascertain the relative contributions of static and dynamic quenching, the non-exponential decays can be characterized as sums of several exponentials or as distribution functions of exponentials, described by organic molecules adsorbed on a number of independently binding sites with different single-exponential lifetimes and relative contributions. For simplicity, those sums of multiple exponentials or distribution functions are calculated to a pre-exponential weighted lifetime (τ_{M0}).¹¹⁻¹⁴ Comparing τ_{M0}/τ_M with I₀/I yields a result that static quenching, if present at all, could account for a few percent of the total quenching only at higher O₂ pressure.¹¹⁻¹⁵ Therefore, regarding the complicated process of O₂ quenching triplet state in solid phase as purely dynamic quenching, further relevant models have been envisaged for addressing the heterogeneous decay kinetics. (see in text)



Figure S5. The fluorescence intensity of compound **2** on the silica gel (porous size of 6 nm in diameter) as a function of O₂ concentration (in % of volume, see text) at temperature (a) 373 K, (b) 298 K and (c) 173 K (λ_{ex} = 350 nm).



Figure S6. The fluorescence intensity of compound **1** on the silica gel (porous size of 6 nm in diameter) as a function of O₂ concentration (in % of volume, see text) at temperature (a) 373 K, (b) 298 K and (c) 173 K ($\lambda_{ex} = 350$ nm).



Figure S7. The fluorescence intensity of compound **3** on the silica gel (porous size of 6 nm in diameter) as a function of O_2 concentration (in % of volume, see text) at temperature (a) 373 K, (b) 298 K and (c) 173 K (λ_{ex} = 350 nm).

[O ₂], %	τ/ns (pre-exp. factor) ^a				
	373 K	298 K	173 K		
0	6.86 (0.93)	7.23 (0.93)	7.21 (0.92)		
	17.88 (0.07)	18.55 (0.07)	19.34 (0.08)		
20	1.86 (0.96)	1.54 (0.92)	0.98 (0.89)		
	7.47 (0.04)	7.35 (0.08)	7.29 (0.11)		
50	0.98 (0.97)	0.90 (0.92)	0.58 (0.85)		
	6.21 (0.03)	6.41 (0.08)	7.19 (0.15)		
100	0.65 (0.97)	0.76 (0.93)	0.48 (0.87)		
	5.93 (0.03)	6.25 (0.07)	6.87 (0.13)		
^a All measurements were recorded under 350 nm excitation wavelength and					
monitored at 480 nm wavelength.					

Table S1. Fluorescence decay dynamics of compound 1 on the silica gel at different temperature.

 Table S2. Fluorescence decay dynamics of compound 3 on the silica gel at different temperature.

[O ₂], %	τ/ns (pre-exp. factor) ^a				
	373 K	298 K	173 K		
0	8.41 (0.92)	8.54 (0.85)	10.27 (0.85)		
	19.85 (0.08)	20.08 (0.15)	22.87 (0.15)		
20	2.58 (0.95)	2.10 (0.85)	1.23 (0.89)		
	8.94 (0.05)	8.75 (0.15)	10.85 (0.11)		
50	1.42 (0.96)	1.27 (0.88)	0.97 (0.90)		
	6.81 (0.04)	7.89 (0.12)	12.46 (0.10)		
100	0.94 (0.97)	0.92 (0.91)	0.78 (0.85)		
	6.51 (0.03)	7.79 (0.09)	12.59 (0.15)		
^a All measurements were recorded under 350 nm excitation wavelength and					
monitored at 520 nm wavelength.					



Figure S8. Plot of the fluorescence intensity ratio (I/I_0) for (a) compound 1 and (b) compound 3 on the silica gel (porous size of 6 nm in diameter) at different temperature as a function of applied O₂ concentration. The solid lines are the best fits using Freundlich model (eq. (2) in text). The dash lines are the best fits using a two-site model (eq. (3) in text).

Table S	3. Fitting	parameters fo	r compound	1 at	different	temperature	using
Freundl	ich model	(eq. (2) in text)					

	373 K	299 K	173 K
1/n	0.72	0.61	0.36
K' _{SV}	0.3461	0.6433	2.1086

Table S4.	Fitting	parameters	for	compound	3 :	at differ	ent t	temperature	using
Freundlic	h model	(eq. (2) in te	xt).						

	373 K	299 K	173 K
1/n	0.66	0.57	0.37
K' _{SV}	0.2828	0.4888	1.2207

Table S5. Fitting parameters	for compound 1 at different temperature using a two
site model (eq. (3) in text).	

	373 K	299 K	173 K		
$f_1{}^a$	0.95	0.93	0.87		
$f_2{}^a$	0.05	0.07	0.13		
K _{SV1}	0.1814	0.3018	1.7194		
K _{SV2}	< 0.0001	0.0021	0.0072		
${}^{a}f_{1}$ and f_{2} are substituted into the approximate pre-exp. factors of two					
decay components respectively shown in Table S1.					

	, ,			
	373 K	299 K	173 K	
f_1^a	0.93	0.90	0.85	
f_2^a	0.07	0.10	0.15	
K _{SV1}	0.1188	0.2120	0.6139	
K _{SV2}	< 0.0001	0.0008	0.0028	
$^{a}f_{1}$ and f_{2}	are substituted int	to the approximate	e pre-exp. factors of	two
decay con	nponents respectiv	vely shown in Tal	ole S2.	

Table S6. Fitting parameters for compound 3 at different temperature using a twosite model (eq. (3) in text).

The observation of CT pathway in O2 quenching triplet state

It is observed that the higher $k_{q obs.}^{T}$, i.e. the ratio of $k_{q obs.}^{T}$ versus the diffusion rate approaching a value of 4/9, correlates well with the more negative free energy change, i, e, ΔG_{CET} for complete electron transfer.¹⁶⁻²¹ This can be interpreted by the fact that the negative ΔG_{CET} gives rise to low lying triplet CT states of O₂-molecule, enhancing the efficiency of O₂ quenching process.

Moreover, upon carefully examining O₂ quenching rate constants for pathway (b) (k_q^3) and pathway (c) (k_q^1) as a function of ΔG_{CET} , a higher degree of the increase in k_q^3 than k_q^1 as ΔG_{CET} becoming more negative was noticed.^{22, 24} This clearly corroborates the relatively more pronounced CT character of pathway (b). Last but not least, an inverse correlation between $k_q^T_{obs.}$ and S_{Δ} signifies a competitive process between CT interaction (pathway (b)) and the generation of singlet oxygen (pathway (c)).²²⁻²⁶

Meanwhile, owing to support the formation of collisional complex in the process of CT state interaction, the temperature dependence of the oxygen quenching process was studied. The activation energy decreases with increasing temperature, approaching a value of zero at high temperatures in the case of triplet quenching, indicating the indeed involvement of exciplexes.²⁷⁻³¹ This result is emphasized in detail in the text.

Partial CT character (pCT) in O2 quenching triplet state

Notwithstanding the strong dependence on ΔG_{CET} making the above CT interaction rational in the course of O₂ quenching triplet state, scientists have cast doubt on the involved process of complete charge transfer, implying that quenching is via complexes with only partial charge transfer.^{24, 31-33} The observation of some electron-withdrawing substituents affecting k_q^T also necessitates a potential barrier ($\Delta G^{\#}$) to charge-transfer formation or the formation of exciplexes with significant CT character in the quenching step.²³ Consequently, applying one common Marcus type to intepret experimental data, Schweitzer et al. have obtained the expected partial CT character (pCT).³⁴

Starting from the following equations:

$$\Delta G_{\rm CT} = f \Delta G_{\rm CET} \tag{4}$$

where f is defined as the corrective factor relating ΔG_{CET} to the free energy change ΔG_{CT} of pCT complex formation in the parabolic model, and

$$\Delta G^{\#} = \frac{\lambda}{4} \left(1 + \frac{\Delta G_{CT}}{\lambda} \right)^2 \tag{5}$$

where $\Delta G^{\#}$ is the driving-force dependence of the activation free energy of an electron transfer step and λ is the reorganization energy, one can obtain f and λ from the phosphors in solvents with different polarities. The $\Delta G^{\#}$ is calculated using eq. (5):

$$\Delta G^{\#} = -RT \ln \frac{k_{CT}}{k_B T/h}$$
(6)

where k_{CT} is the rate constant of the triplet pCT deactivation pathway, obtaining from empirical data; k_B and h are the Boltzmann and Planck constants; T is the Kelvin temperature. The satisfactory fitting results showed that both f and λ increase with increasing solvent polarity. With further analysis of the degree of charge transfer (δ) contributing to λ , which can be expressed as a function of a dipole moment relating the solvent polarity, the value of δ should be larger than 0.25 to correlate well with the realistic value of λ . Therefore, it is concluded that the pCT character is shown to be significantly larger than 25% and to increase with increasing solvent polarity.

The investigation on the pathways in O2 quenching singlet state

From the energetics point of view, pathway (d) (see **Scheme 5** in text) requires S_1 - T_1 energy gap of M to be > 7883 cm⁻¹, the zero-point energy of the lowest excited state of singlet molecular $O_2(^{1}\Delta_g)$. However, molecules even having S_1 - T_1 energy gap less than the required energy are susceptible to O_2 fluorescence quenching,³⁵⁻³⁶ which instead is reported to depend on the energy difference between S_1 and T_2 .^{32, 37} Conceivably, pathway (d) is not the only or predominant mechanism of O_2 quenching singlet state.

As for the other two possibilities, it has long been accepted that O_2 quenching fluorescence proceeds exclusively via pathway (f), which occurs by a simple enhancement of intersystem crossing to the triplet state due to increased S_1 - T_n mixing in the O₂-aromatic complex,^{36, 38-40} while pathway (e) is first thought to be unfavorable because the observed internal conversion has negligible contribution to the overall deactivation of S_1 ,^{38, 41-42} only except for 9,10-diphenylanthracene.⁴³ Recently, research has also provided that in study of some β -Carboline alkaloids, O₂-induced $S_1 \rightarrow S_0$ internal conversion can efficiently compete with O₂-induced $S_1 \rightarrow T_1$ intersystem crossing.⁴⁴⁻⁴⁵ Hence, the process of O₂ quenching fluorescence may consist of pathway (d)-(f).

	τ_0^T / μs	τ^T / μs	$k_q^T / 10^3 \text{ torr}^{-1} \cdot \text{s}^{-1}$		
Pd1 ^a	90.84	3.845	1.64		
Pd2 ^a	198.3	2.947	2.19		
Pt1 ^a	1.479	0.909	2.79		
Pt2 ^a	2.356	0.790	5.54		
PdOEP ^b	1000		9.45		
PtOEP ^b	97.8		4.09		
PtTFPP ^b	76.9		4.77		
PtTPP ^b	81.4		7.19		
[Ru(dpp) ₃]Cl ₂ ^b	8.14		7.86		
[Ru(phen) ₂ phenCH ₃]Cl ₂ ^b	5.84		25.1		
[Ru(phen) ₃]Cl ₂ ^b	4.54		33.5		
$[Ru(bpy)_3]Cl_2^b$	1.74		18.1		
^a Data from Ref. 109 in text. k_q^T are calculated by eq. (10) in text with $[O_2]=20\%$.					
^b Data from Ref. 27. Because τ^T are not shown in Ref. 27, k_q^T are calculated					
from Stern-Volmer constant.					

Table S7. The calculated \mathbf{k}_q^T for reported transition-metal complex in solid phase at room temperature.



Figure S9. Fluorescence decay dynamics of (a) compound 1, (b) compound 2 and (c) compound 3 under 0% and 20% O₂ in ethanol at room temperature.

8 1 ()			
	$\tau_0^S \ /ns$	$ au^S$ $/ns^a$	$k_q^S /10^{10} { m M^{-1} \cdot s^{-1}}$
Compound 1 ^b	10.52	8.04	5.13
Compound 2 ^c	4.61	4.05	5.27
Compound 3 ^d	10.59	8.13	5.01

Table S8. The calculated k_q^S for compound 1-3 in ethanol at room temperature using eq (9) in text.

^aThe data were measured under $[O_2]=20\%$.

^bThe data were recorded under 377 nm excitation wavelength and monitored at 500 nm wavelength.

^cThe data were recorded under 377 nm excitation wavelength and monitored at 520 nm wavelength.

^dThe data were recorded under 377 nm excitation wavelength and monitored at 570 nm wavelength.

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