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Electronic Supplementary Information

Molecular design toward suppressing electron recombination and enhancing light-absorbing ability of dye for sensitized solar cell: A theoretical investigation

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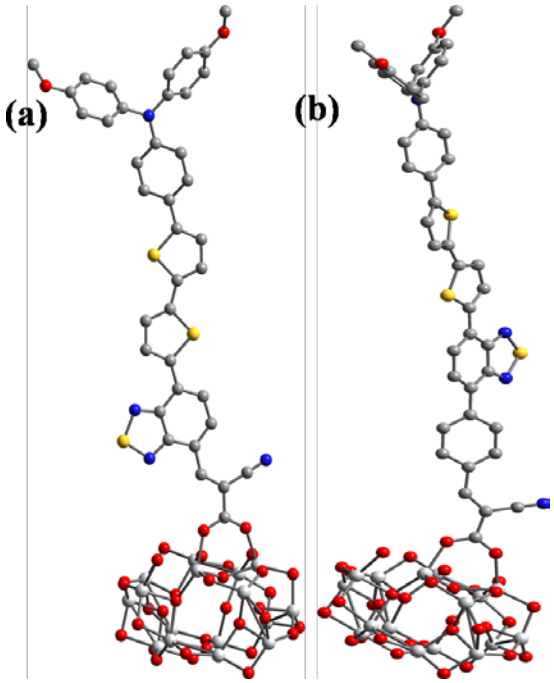
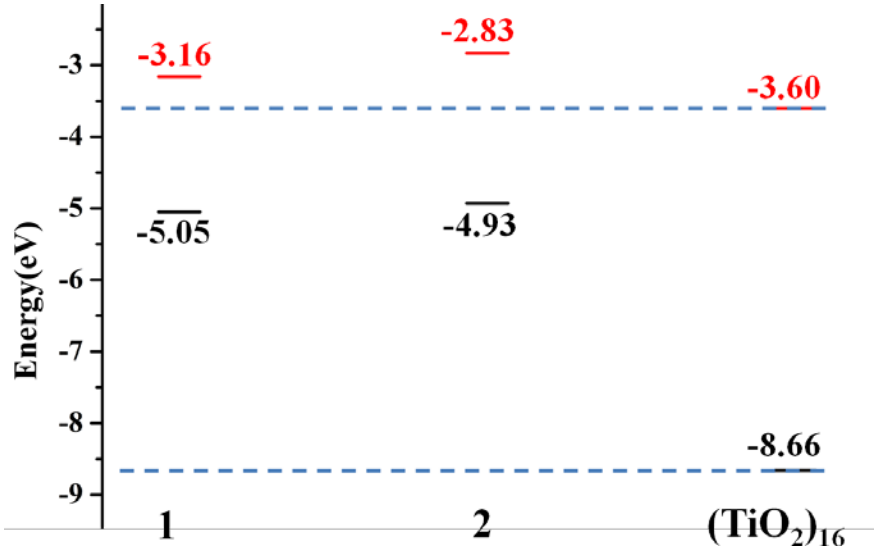


The geometry of dye-TiO_2 (neutral TiO_2, neutral dye) is obtained from attaching dye with TiO_2 cluster followed by optimization. The structure of dye$^+$-TiO_2 (neutral TiO_2, cationic dye), a pre-optimized cationic dye is fitted into pre-optimized dye-TiO_2 without further optimization.

Fig. S1 Structures of dye-TiO_2 complex for (a)**1$^+$-TiO$_2$** and **2$^+$-TiO$_2$.**



The optimization of $(TiO_2)_{16}$ was done at PBE0/6-31G(d, p) level with Gaussian program. The calculated LUMO energy levels of the dyes are above the conduction band of $(TiO_2)_{16}$, and the HOMOs of the dyes are in the gap of $(TiO_2)_{16}$, thus we can use the cluster for electronic processes responsible for DSSC functionality.

Fig. S2 Calculated energy levels for $(TiO_2)_{16}$ cluster and dyes **1** and **2.**

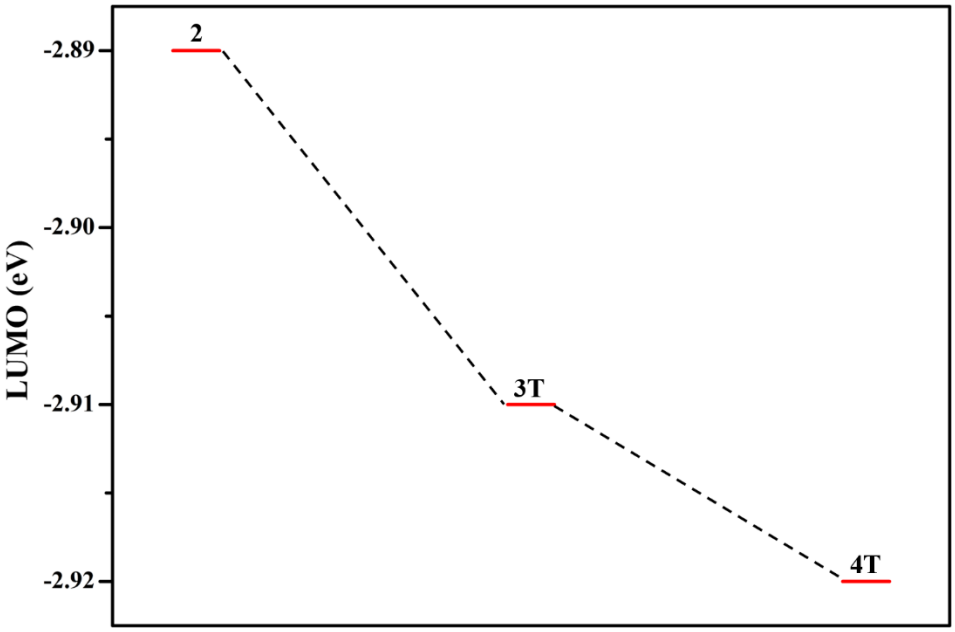
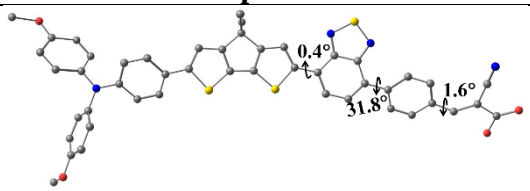
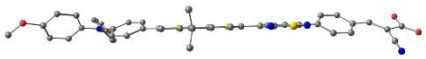
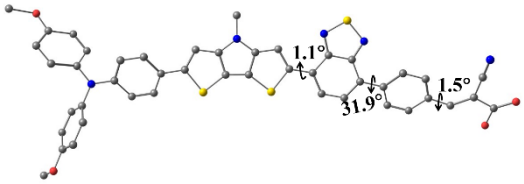
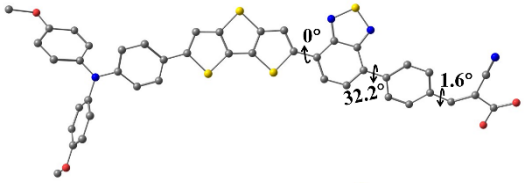
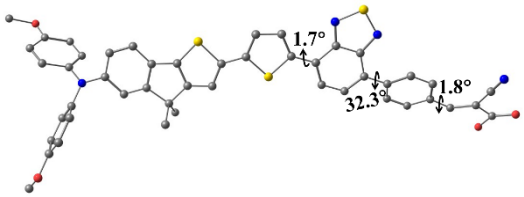
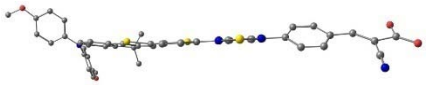
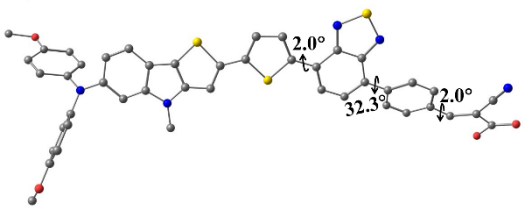
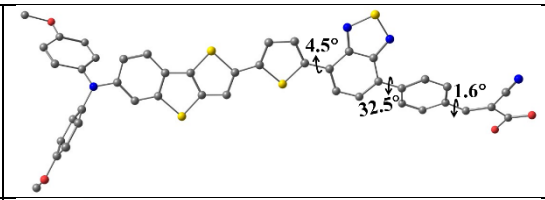
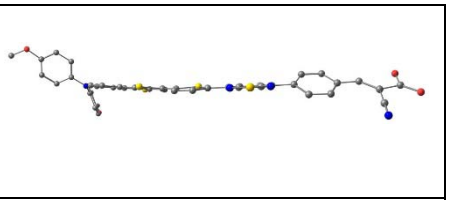
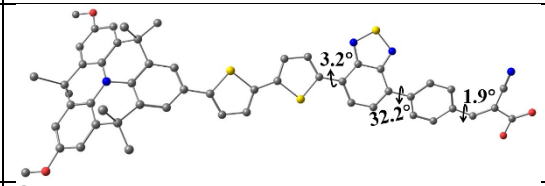
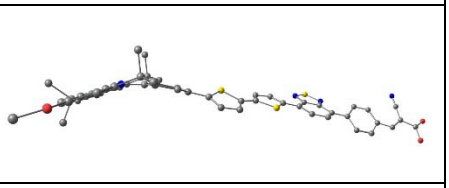
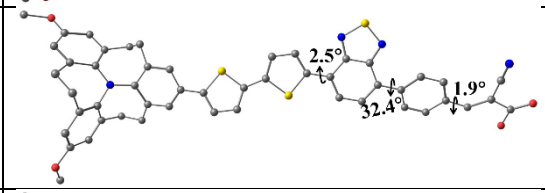
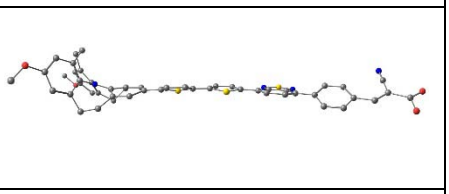
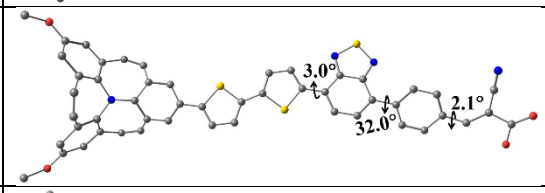
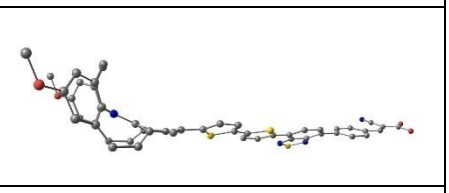
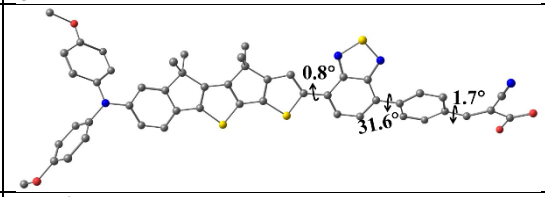
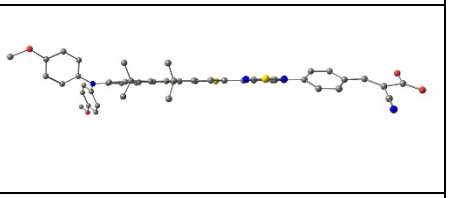
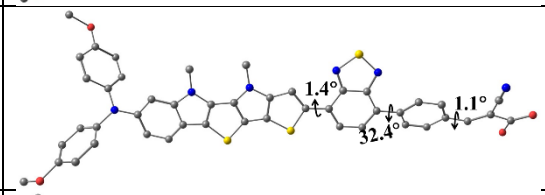
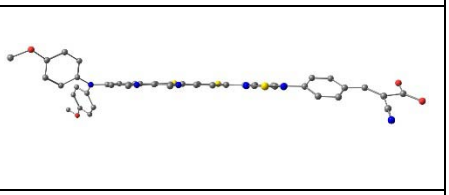
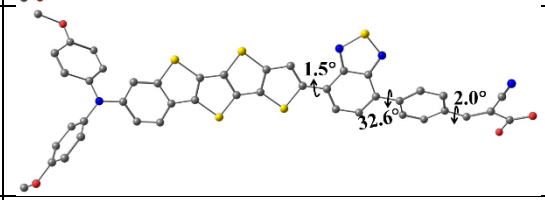
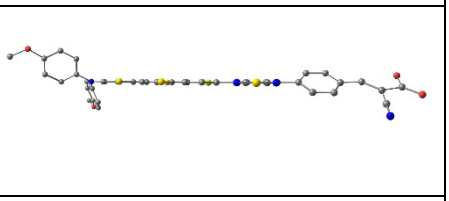
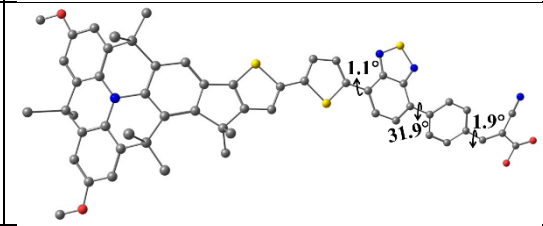
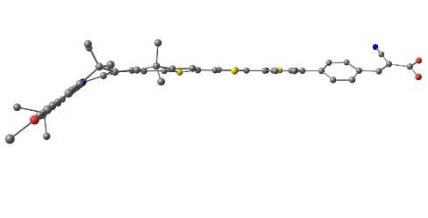
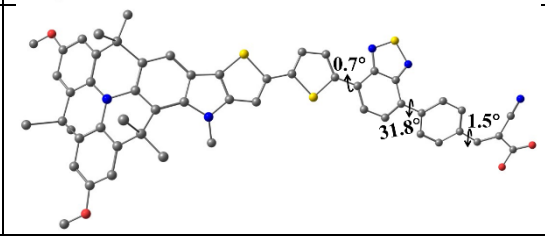
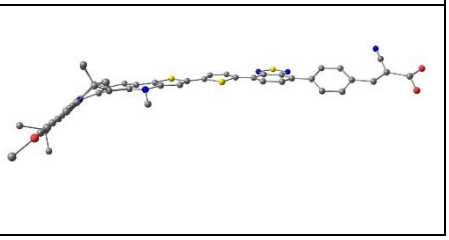


Fig. S3 Calculated LUMO levels for the dyes **2**, **3T** and **4T**.

Dye	Top view	Side view
A1		
A2		
A3		
B1		
B2		

B3		
C1		
C2		
C3		
D1		
D2		
D3		
E1		
E2		

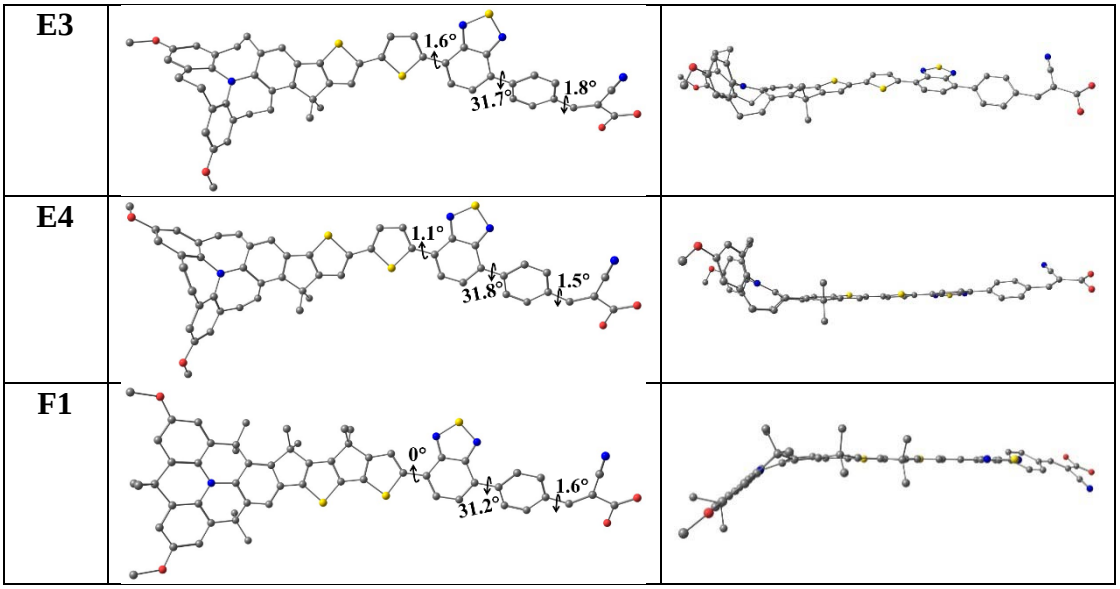


Fig. S4 Optimized structures of all the designed dyes from top and side views.

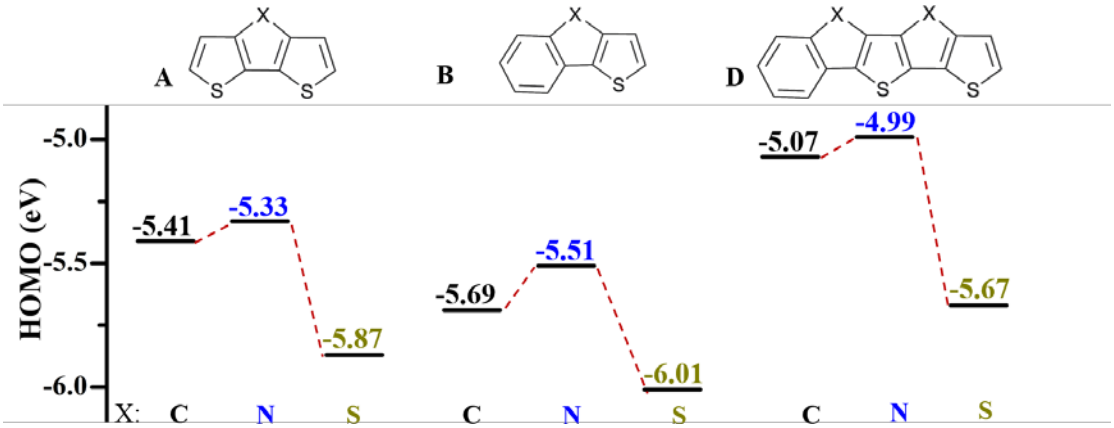


Fig. S5 Calculated energy levels of HOMO for the series dyes **A**, **B** and **D**.

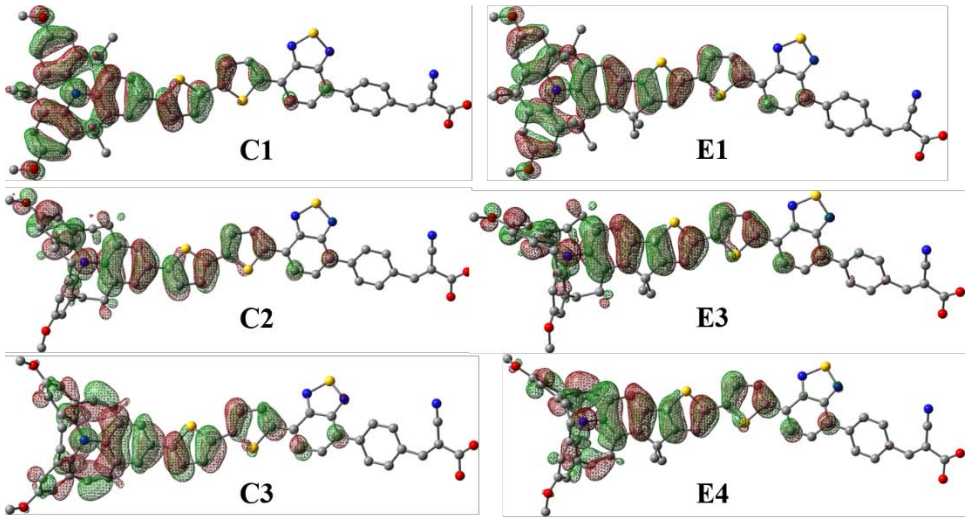


Fig. S6 Spatial distributions of HOMO of some selected dyes (Saturated H atoms are not shown).

Table S1 Calculated HOMO energy levels of dyes **1** and **2** in dichloromethane (CH_2Cl_2) with functionals of B3LYP, PBE0 and PBE38, and corresponding experimental values. (Unit: eV)

	B3LYP (20% HF_{exc})	PBE0 (25% HF_{exc})	PBE38 (37.5% HF_{exc})	Exp.
1	-4.81	-5.05	-5.47	-5.22
2	-4.75	-4.93	-5.44	-5.14

Table S2 Effects of the functional used on the maximum absorption wavelengths (λ_{max}, nm) of dyes **1** and **2** in CH_2Cl_2 solution, with available experimental results. The values denote the percentage of nonlocal Hartree-Fock exchange (HF_{exc}) in parentheses.

	B3LYP (20%)	PBE0 (25%)	PBE0-1/3 (33.3%)	MPW1K (42.8%)	BHandHLYP (50%)	CAM-B3LYP (19-65%)	ωB97XD (22-100%)	Exp.
1	900	809	693	608	570	548	519	570
2	777	697	602	537	509	491	468	515

Table S3 Computed Q_{HOMO}, maximum absorption wavelengths (λ_{max}, nm), excitation energies ($E_{\lambda max}$, eV), oscillator strengths (f), light harvesting efficiency (Φ_{LHE}), normalized integrated spectral area (S) and the lifetimes τ of the S_1 excited state for the designed dyes **3T**, **4T** and reference dye **2**.

Compd.	Q_{HOMO}(%)	λ_{max}	$E_{\lambda max}$	f	Φ_{LHE}	S	τ($\times 10^{-9}$ s)
2	0.25	509	2.43	1.84	0.99	1	2.13
3T	0.14	519	2.39	2.20	0.99	1.29	1.84
4T	0.08	519	2.39	2.57	0.99	1.55	1.58

Table S4 Computed energy levels of LUMO, the lifetimes τ of the S_1 excited state and dominant excitations corresponding to $S_0 \rightarrow S_1$ for the series dyes **A**-**F**.

Compd.	LUMO	$E_{\lambda max}$	r^2	τ($\times 10^{-9}$s)	Transition and composition
A1	-2.77	2.24	33.54	2.49	H→L (0.68); H-1→L (0.18)
A2	-2.75	2.27	32.74	2.47	H→L (0.71); H-1→L (0.17)
A3	-2.86	2.44	30.76	2.10	H→L (0.58); H-1→L (0.29)
B1	-2.82	2.31	32.34	2.36	H→L (0.64); H-1→L (0.21)
B2	-2.83	2.30	31.26	2.48	H→L (0.66); H-1→L (0.19)
B3	-2.88	2.42	31.74	2.09	H→L (0.58); H-1→L (0.27)
C1	-2.83	2.41	31.04	2.19	H→L (0.53); H-1→L (0.32)

C2	-2.81	2.41	31.24	2.16	H→L (0.61); H-1→L (0.24)
C3	-2.80	2.32	32.70	2.31	H→L (0.64); H-1→L (0.21)
D1	-2.76	2.15	35.57	2.68	H→L (0.73); H-1→L (0.14)
D2	-2.77	2.19	32.39	2.77	H→L (0.74); H-1→L (0.15)
D3	-2.90	2.44	31.89	2.03	H→L (0.61); H-1→L (0.26)
E1	-2.80	2.25	32.89	2.52	H→L (0.66); H-1→L (0.19)
E2	-2.83	2.24	36.61	2.58	H→L (0.68); H-1→L (0.17)
E3	-2.78	2.24	33.26	2.53	H→L (0.71); H-1→L (0.15)
E4	-2.76	2.17	34.10	2.69	H→L (0.72); H-1→L (0.14)
F1	-2.74	2.10	36.27	2.81	H→L (0.73); H-1→L (0.14)

Table S5 Calculated Λ, ΔG^0, EXP and $\frac{exp}{\sqrt{\Lambda}}$ values for reference dye **2** and dyes **A1**, **B1** and **C1**.

Dye	Λ_{in}	Λ_{out}	Λ	ΔG^0	EXP	$\frac{exp}{\sqrt{\Lambda}}$
2	0.114	0.544	0.658	-0.712	0.990	1.22
A1	0.115	0.508	0.623	-0.594	0.987	1.25
B1	0.096	0.509	0.605	-0.577	0.987	1.27
C1	0.114	0.514	0.628	-0.553	0.916	1.16

On the calculation of the lifetime (τ) of the S_1 excited state

The lifetime of spontaneous luminescence for the dyes are evaluated approximately by the formula:[1, 2]

$$\tau = \frac{1}{A_{k,k'}},\ A_{k,k'} = \frac{4e^2\Delta E_{k,k'}^3}{3\hbar^4 c^3}\left|r_{k,k'}\right|^2$$

where $A_{k,k'}$ is Einstein coefficient for spontaneous emission, *e* is the elementary charge, $\hbar$ is the reduced Planck′s constant, and *c* is the speed of light in vacuum, $\Delta E_{k,k'}$ and $r_{k,k'}$ represent the transition energy and transition dipole moment from states k to k′, respectively.

References:

1 L.-N. Yang, Z.-Z. Sun, S.-L. Chen and Z.-S. Li, *Dyes Pigments*,2013, **99**, 29 – 35.
2 S.-L. Chen, L.-N. Yang and Z.-S. Li, *J. Power Sources*, 2013,**223**, 86 – 93