Two-photon absorption and polymerization ability of intramolecular energy transfer based photoinitiating systems†

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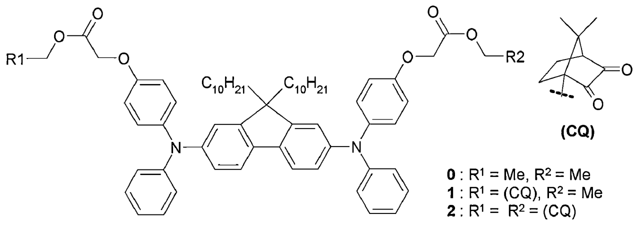
We design a new photoinitiating system where the two-photon absorption of a 2,7 bisaminofluorene moiety leads to the photoactivation of a camphorquinone subunit through a Förster-type intramolecular energy transfer: the application to a two-photon polymerization reaction is demonstrated.

The potential and promising applications[1–6] of multi-photon absorption spectroscopy in high density optical data storage, 3D micro-nanofabrication, power limiting, fluorescence microscopy, photodynamic therapy has strongly stimulated the research for the elaboration of modular architectural macrosystems combining both large two-photon absorption 2PA cross sections (δ) and desired photo activated properties. In the case of applications involving a two-photon initiated polymerization reaction, the introduction of an efficient photoinitiator PI is necessary.[1,7] Commercial PIs, however, exhibit very poor δ and cannot be efficiently excited according to a 2PA process.[8] In the present paper, we propose a new approach based on the design of a PS-PI linked photoinitiating system where PS is a photosensitizer that must exhibit a large δ and lead to an excited state of PI through an intramolecular energy transfer process. This is illustrated by the following PS-PI system (Scheme 1).

It consists in a 2,7-bis(diphenylamino)fluorene **FL** moiety as an energy donor (PS) and camphorquinone **CQ** (PI) as an energy acceptor. **CQ** is a UV-visible absorbing molecule that is largely used, when combined with tertiary amines, in radical photopolymerization.[8–11] Moreover, its efficiency is weakly affected by oxygen[9,12,13] which constitutes a relevant asset for 3-D stereolithography. Fluorene derivatives exhibit relatively large 2PA cross-sections and can efficiently absorb NIR light.[14–16]

Furthermore, **FL** fluoresces within the absorption spectral range of **CQ**. As a result, the introduction of **FL** should generate the excited state **CQ*** upon 2PA.

Herein, we report on the photophysical and photochemical properties of this new generation of 2PA working photoinitiators. Both the energy transfer efficiency and the two-photon absorption properties of **1** and **2** will be discussed in comparison with the model molecules **0** and **CQ**.



Scheme 1

The absorption spectra of compounds **0–2** (Fig. 1) show the typical features[14–16] of the **FL** moiety with maximum at 375 nm in the acetonitrile and similar extinction coefficients (ε_{max} = 3.6 × 10^4 mol^{-1} L cm^{-1}). They exhibit a small shoulder in the 420–475 nm wavelength range corresponding to the strongly forbidden n–π* electronic transition of **CQ** (ε_{475} = 36.8 mol^{-1} l cm^{-1}).[17] The latter band is twice higher for **2** than for **1** as a consequence of the number of camphorquinone units.

The fluorescence emission spectra, located in the 370–560 nm region, are slightly red shifted when going from cyclohexane to acetonitrile (Fig. 1 and Table 1): this suggests a low dipole moment for the emitting excited states consistent with the specular symmetry of the **FL** unit.[7] However, both the emission quantum yields and the fluorescence lifetimes of **FL** strongly decrease from **0** to **1** or **2**. For example, this leads to a quenching efficiency of 93% in cyclohexane and 95% in acetonitrile for **1**. In contrast with the strong quenching observed for the emission of **1** or **2** with respect to fluorescence

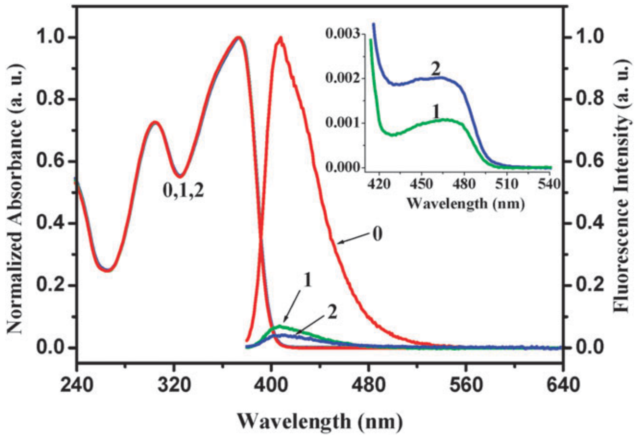


Fig. 1 Normalized steady-state absorption and fluorescence spectra of compounds **0**, **1** and **2** in acetonitrile at room temperature. Inset: spectra in the 410–540 nm region showing the absorption of the camphorquinone chromophores in compounds **1** and **2** (c = 2.8 × 10^{-6} mol. L^{-1}).

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Table 1 Absorption and fluorescence properties

	Cyclohexane				Acetonitrile			
	λ_{abs}/nm	λ_{fluo}/nm	$\Phi_f{}^a$	$\tau_f{}^b$/ns	λ_{abs}/nm	λ_{fluo}/nm	$\Phi_f{}^a$	$\tau_f{}^b$/ns
0	380	397	0.31	0.98	375	408	0.46	1.42
1	380	397	0.02	0.10	375	409	0.03	0.11
2	380	397	0.01	0.20	374	409	0.02	0.12

[a] Fluorescence quantum yields. [b] Fluorescence lifetimes measured by time correlated single photon counting (TCSPC) at $\lambda_{fluo}{}^{max}$.

of **0**, addition of **CQ** to a solution of **0** hardly affects the fluorescence intensity of **0**, the quenching coefficient has a value of 90 M^{-1} in cyclohexane. The absence of solvent polarity effect on fluorescence of **1** or **2** excludes any excited charge transfer mechanism. A through-bond Dexter-type energy transfer is also ruled out due to the presence of the methylene spacer between the subunits, as considered in other systems.[3,18] Thus, the fluorescence quenching in **1** and **2** is attributed to a Förster-type energy transfer from the absorbing **FL** moiety to the **CQ** chromophore. The corresponding Förster radius[19] calculated from the overlap integral between the absorption and the fluorescence bands of **CQ** and compound **0** leads to a value of 15 Å (see ESI,† Fig. S1). Such a distance appears as an upper limit when compared to the values ($\cong$13 Å) calculated by AM1 geometric optimization of **1** and **2**. The very weak fluorescence of the **CQ** moiety ($\phi_f = 0.0029$)[13] whose maximum emission wavelength is located at 530 nm cannot be collected in the steady state experiments because of the overlap with the residual emission of **FL**. TCSPC experiments allows one to detect a new long component (16 ns) in the fluorescence decays of **1** and **2** at 530 nm (see ESI,† Fig. S2) as the one observed in the case of **CQ** which well confirms the subsequent generation of ^{1}**CQ***.

The time-gated structured phosphorescence spectra of **CQ**, **1** and **2** in EPA (diethyl ether–isopentane–ethanol (4 : 4 : 1 v/v)) glassy matrix at 77 K are perfectly similar (Fig. 2). The corresponding excitation spectra taken at the maximum emission wavelength, however, are totally different. The characteristic absorption bands at 450 nm and 375 nm arising from **CQ** and **2**, respectively, are observed. This definitively supports the energy transfer from the **FL** moiety and confirms the formation of a low lying triplet state centred on **CQ**. The intersystem crossing quantum yields of **1** and **2** (using **CQ** as an actinometer)[13] are evaluated as *ca.* 0.35.

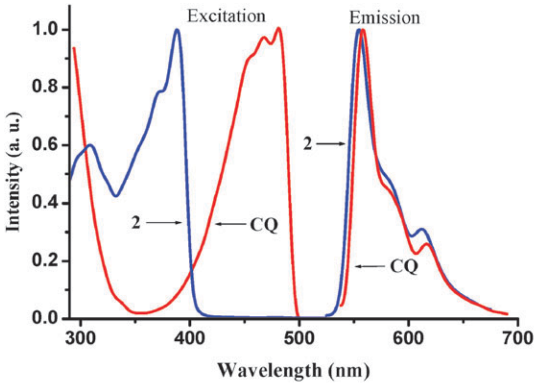

Fig. 2 Phosphorescence excitation and emission spectra of **CQ** and compound **2** in an EPA glassy matrix at 77 K.

Energy transfer is also supported by nanosecond laser flash photolysis. Laser excitation of **1** and **2** in acetonitrile at 266 nm leads to a transient absorption around 800 nm (see ESI,† Fig. S3) similar to that observed under the direct excitation of **CQ** already ascribed to ^{3}**CQ**.[9,12,13] In the same experimental conditions, the ^{3}**CQ** moiety absorbance in **1** and **2** is noticeably lower than that measured in **CQ** itself, consistent with a lower intersystem crossing quantum yield.

The 2PA cross-sections were determined by the two-photon-induced fluorescence method,[20,21] relatively to coumarin 480 in methanol.[22] The quadratic relationship between the fluorescence intensity and the excitation power confirms the two-photon absorption regime. The insert in Fig. 3 shows the 2PA spectra of **0–2** in acetonitrile. Each compound exhibits a similar spectrum with an intense band below 690 nm (>300 GM) and a shoulder at 740 nm in a very good agreement with the very recent 2PA spectra obtained from an open aperture Z-scan method.[23] Moreover, the quenching efficiency of the 2PA induced fluorescence of the **FL** moiety in **1** and **2** is 95% as observed in the one-photon absorption measurements: this clearly demonstrates that the two-photon absorption is also followed by an efficient intramolecular energy transfer process.

Finally, the fabrication of 20 μm width lines (Fig. 3) was achieved by focusing a femtosecond pulsed laser beam (Ti:Sapphire laser; λ_{exc} = 750 nm; average power: 1.2 mW) into a diacrylate monomer (Sartomer SR344) containing **2** as a photoinitiator (0.5% wt.) and *N*-methyl(*N*,*N*′-diethanol)-amine (MDEA) as co-initiator (3% wt.). The presence of MDEA (as the interaction of the two-photon excited

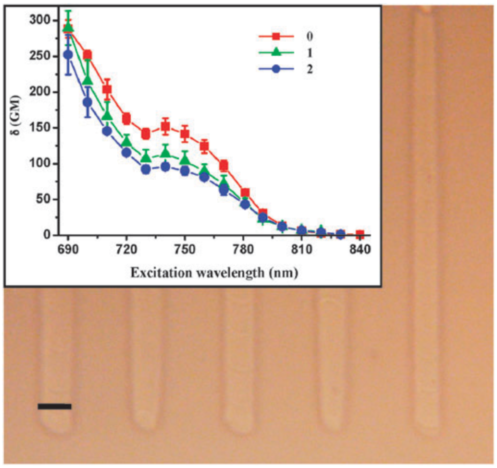

Fig. 3 Lines produced by 2PA polymerization of a diacrylate matrix. Scale bar: 20 μm. The low resolution is due to the available exposure and analysis device. Inset: 2PA spectra of **0–2** in acetonitrile.

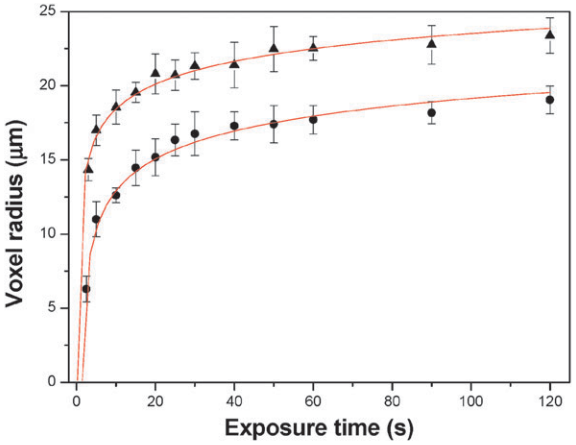

Fig. 4 Variation of the polymerized voxel radius as function of exposure time (concentration of both chromophores: 4×10^{-3} M, circles: compound **0**, triangles: compound **2**, average power: 0.7 mW). The solid lines correspond to the best fit data using equation in ref. 25 (see ESI†).

camphorquinone derivative with MDEA yields the initiating aminoalkyl radical) was necessary to observe the polymerization.

In the same condition, the reference compound **0** also leads to two-photon polymerization (see ESI,† Fig. S4). In this case, photoinitiating process is assumed[1,24] to proceed through an electron transfer from photoexcited **0** to acrylate monomer which produces a radical cation that is subsequently used as hydrogen abstractor reactant. However for compound **0**, the threshold of two-photon polymerization measured by point-by-point exposure method[5,25,26] exhibits a relative value that is 5.8 times higher than that measured for compound **2** (Fig. 4).

The substantial improvement of the two-photon polymerization efficiency corroborates the occurence of a distinctive photoinitiating process for compounds **1** or **2** with the involvement of the camphorquinone subunit. Therefore, we have a clear demonstration of an effective two-photon initiated polymerization.

In conclusion, the design of covalently bonded PS-PI structure working through energy transfer seems promising for the development of efficient two-photon photoinitiating systems for free radical photopolymerization. The main interest lies on the fact that the initiation mechanism will be obviously the same as under the usual one-photon absorption. The finding of other suitable combinations of a molecular skeleton possessing ever higher δ with an efficient PI is a fascinating challenge.

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