Electronic Supporting Information

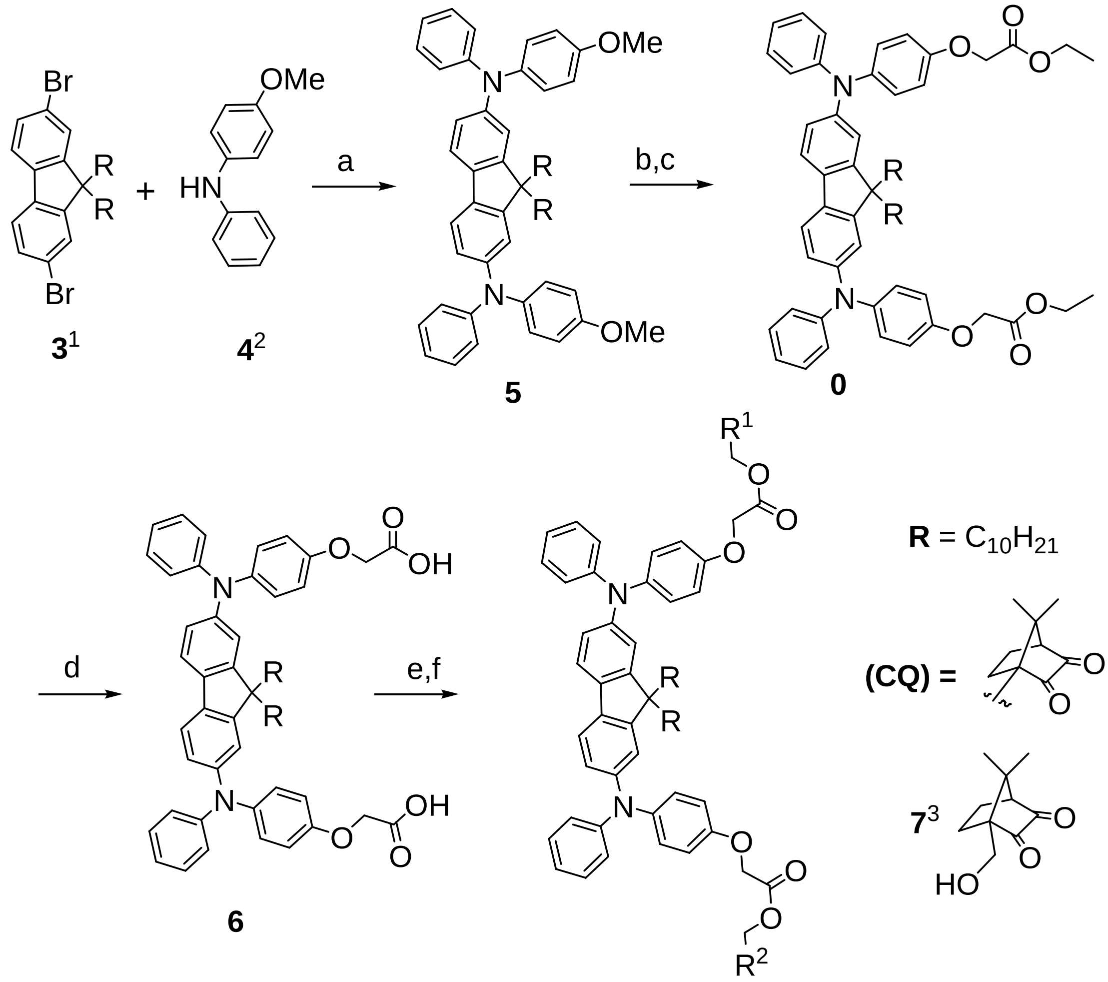
Two-photon Absorption and Polymerization ability of Intramolecular Energy Transfer Based Photoinitiating Systems

Ming Jin,[§] Jean-Pierre Malval,*[,§] Davy-louis Versace,[§] Fabrice Morlet-Savary,[§] Hélène Chaumeil,[‡] Albert Defoin,[‡] Xavier Allonas,[§] and Jean-Pierre Fouassier[§]

[§]Département de Photochimie Générale, CNRS UMR 7525, and [‡]Laboratoire de Chimie Organique et Bioorganique, CNRS UMR 7015.

Ecole Nationale Supérieure de Chimie de Mulhouse, 3 rue Alfred Werner, 68093 Mulhouse Cedex, France E-mail : jean-pierre.malval@uha.fr

Scheme 1. Synthetic routes of the compounds **0, 1, 2.**



1 R^1 = (CQ), R^2 = Me, 18 %
2 R^1 = R^2 = (CQ) , 15%

Conditions: a) $Pd_2(dba)_3$, P*t*Bu_3, KO*t*Bu, Toluene, 70°C, 16 h, 85 %. b) BBr_3, CH_2Cl_2, -78°C, 2 h, rt, 2 h, 87 %. c) $BrCH_2COOEt$, K_2CO_3, EtOH, 60°C, 2 d, 98 %. d) NaOH, 1,4-Dioxane/ H_2O, rt, 1 d, 100%. e) $ClCO_2Et$, NEt_3, THF, 30 mn, 0°C. f) **7**, NEt_3, THF, rt, 24 h.

Physical data for the compounds 0, 1, 2.

Compound 0: colorless resin.

ν $_{max}$(KBr)/cm^{-1} 2925, 2853, 1763, 1739, 1594, 1506, 1467, 1439, 1272, 1193, 1084, 1029, 827, 750, 696.

δ_H (C_6D_6, 400 MHz, 295 K) 0.88 (t, *J* 7.2, 6 H), 0.91 (t, *J* 6.5, 6 H), 0.93 (m, 4 H), 1.10 (m, 8 H), 1.24 (m, 20 H), 1.68 (m, 4 H), 3.89 (q, *J* 7.2, 4 H), 4.20 (s, 4 H), 6.74 (d, *J* 8.8, 4 H), 6.86 (t, *J* 7.2, 2 H), 7.07-7.15 (m, 10 H), 7.21 (d, *J* 7.8, 4 H), 7.29 (d, *J* 1.8, 2 H), 7.38 (d, *J* 8.3, 2 H);

δ_C (C_6D_6, 100.6 MHz, 295 K) 14.10, 14.41, 23.13, 24.57, 29.81, 29.89, 30.09, 30.15, 30.53, 32.36, 40.47, 55.34, 60.85, 65.85, 116.06, 118.80, 120.33, 122.26, 123.17, 123.41, 126.86, 129.54, 136.36, 142.43, 147.34, 149.02, 152.48, 154.87, 168.40;

HRMS (ESI-MicroTOF) *m/z* 984.5980 (M$^+$). $C_{65}H_{80}N_2O_6$ requires: 984.6016.

Anal calcd for $C_{65}H_{80}N_2O_6$ (985.34): C, 79.23, H, 8.18, N, 2.84. Found: C, 79.3, H, 8.2, N, 2.9.

Compound 1: greenish resin;

ν $_{max}$(KBr)/cm^{-1} 2926, 2854, 1758, 1594, 1506, 1492, 1466, 1439, 1272, 1193, 1082, 1029, 826, 750, 696;

δ_H(C_6D_6, 400 MHz, 295 K) 0.43 (s, 3 H), 0.57 (s, 3 H), 0.87 (t, *J* 7.2, 3 H), 0.93 (m, 12 H), 1.10 (m, 8 H), 1.25 (m, 22 H), 1.69 (m, 4 H), 2.00 (d, J 4.8, 1 H), 3.88 (q, *J* 7.2, 2 H), 4.20 (s, 4 H), 4.24 (s, 2 H); 6.73, 6.77 (2 d, *J* 9.1, 4 H); 6.87, 6.89 (2 t, *J* 6.5, 2 H), 7.07-7.18 (m, 10 H); 7.22, 7.23 (2 d, *J* 7.6, 4 H), 7.32, 7.33 (2 d, *J* 2.0, 2 H); 7.39,7.41 (2 d, *J* 8.3, 2 H);

δ_C(C_6D_6, 100.6 MHz, 295 K) 14.09, 14.41, 17.69, 21.44, 21.57, 23.13, 24.58, 25.53, 29.81, 29.91, 30.08, 30.15, 30.55, 32.36, 40.49, 42.36, 55.36, 58.61, 60.10, 60.73, 60.84, 65.48, 65.85, 115.84, 116.07, 118.77, 120.35, 122.29, 122.35, 123.15, 123.43, 126.88, 126.94, 129.54, 129.58, 136.30, 136.46, 142.42, 142.57, 147.27, 147.40, 149.01, 152.47, 152.54, 154.54, 154.88, 168.37, 200.61, 200.65;

HRMS (ESI-MicroTOF) *m/z* 1120.6458 (M$^+$). $C_{73}H_{88}N_2O_8$ requires 1120.6541.

Anal calcd for $C_{73}H_{88}N_2O_8$ (1121.49): C, 78.18, H, 7.91, N, 2.50. Found: C, 78.3, H, 7.9, N, 2.5.

Compound 2. Yellowish crystals, mp 60-62°C;

ν_{max}(KBr)/cm^{-1} 2935, 2853, 1758, 1594, 1506, 1493, 1467, 1439, 1272, 1187, 1080, 696;

δ_H(C_6D_6, 400 MHz, 295 K) 0.43 (s, 6 H), 0.57 (s, 6 H), 0.93 (m, 14 H), 1.10 (m, 8 H), 1.25 (m, 24 H), 1.69 (m, 4 H), 2.00 (d, *J* 4.8, 2 H), 4.20 (s, 4 H), 4.24 (s, 4 H), 6.73 (d, *J* 8.8, 4 H), 6.89 (t, *J* 6.2, 2 H), 7.09-7.18 (m, 10 H), 7.23 (d, *J* 7.6, 4 H), 7.33 (d, *J* 1.8, 2 H), 7.41 (d, *J* 8.3, 2 H);

δ_C(C_6D_6, 100.6 MHz, 295 K) 14.42, 17.69, 21.45, 21.57, 23.14, 24.60, 25.53, 29.82, 29.92, 30.10, 30.16, 30.57, 32.37, 40.51, 42.37, 55.39, 58.61, 60.11, 60.74, 65.48, 115.85, 118.75, 120.37, 122.39, 123.15, 123.45, 126.96, 129.59, 136.40, 142.56, 147.33, 149.00, 152.53, 154.56, 168.37, 200.61, 200.65;

HRMS (ESI-MicroTOF) *m/z* 1256.7202 (M^+). $C_{81}H_{96}N_2O_{10}$ requires 1256.7065.

Anal calcd for $C_{81}H_{96}N_2O_{10}$ (1257.64): C, 77.36, H, 7.69, N, 2.23. Found: C, 77.6, H, 7.9, N, 2.2.

Spectroscopy.

All spectroscopic measurements were performed in spectrophotometric grade solvents from Aldrich and Fluka. UV-Visible absorption spectra were recorded with a Perkin-Elmer spectrophotometer. Extinction coefficients, ε_{max}, were measured on multiple solutions obtained by dilution of two or three stock solutions. The measurements were performed using cuvettes with path lengths between 0.025 and 1 cm.

Steady state fluorescence and phosphorescence spectra were collected using a FluoroMax IV spectrometer. The quantum yields, Φ, (which took into account the correction due to the solvent refractive index) were determined in optically dilute solutions using anthracene in ethanol as reference[1].

The fluorescence lifetimes were measured using a Nano-LED emitting at 372 nm as an excitation source with a nano-led controller module, Fluorohub from IBH, operating at 1 MHz. The detection was based on an R928P type photomultiplier from Hamamatsu with high sensitivity photon-counting mode. The decays were fitted with the iterative reconvolution method on the basis of the Marquardt/Levenberg algorithm[2]. Such a reconvolution technique allows an overall-time resolution down to 0.1 ns.

Energy transfer mechanism.

The extent of the Förster energy transfer between a donor and an acceptor can be evaluated via the Förster radius, R_0, which identifies the distance at which transfer occurs with 50% probability. $\mathbf{R_0}$ is given by equation. (1) [3, 4]

$$R_0 = \frac{0.5291 f^2 \Phi_D}{n^4 N_A} . J_{DD} \qquad (1)$$

where f^2 is an orientation factor (2/3 for randomly oriented molecules), **n** is the refractive index of the medium, $\mathbf{N_A}$ the Avogadro number and Φ_D is the fluorescence quantum yield of the donor, here, it should be compound **0**. J_{DD} is the spectral overlap integral, defined as in equation (2)

$$J_{DD} = \int_0^{\infty} \frac{\varepsilon_A(\nu) F_D(\nu)}{\nu^4} . d\nu \qquad (2)$$

where ε_A is the molar absorption coefficient spectrum of the acceptor (here, camphorquinone, **CQ**), **ν** the energy in wavenumbers and $\boldsymbol{F_D(\nu)}$ the normalised emission spectrum ($\int F_D(\nu)d\nu = 1$). From the normalised emission spectrum of compound **0** and the molar extinction coefficient spectrum of **CQ** as shown in Figure S.1, $\boldsymbol{R_0}$ is calculated to be ca. 15 Å. This value appears as an upper limit in comparison with the mean molecular radius of compounds **1** and **2** (≈ 13 Å) obtained from AM1 geometric optimization[5]

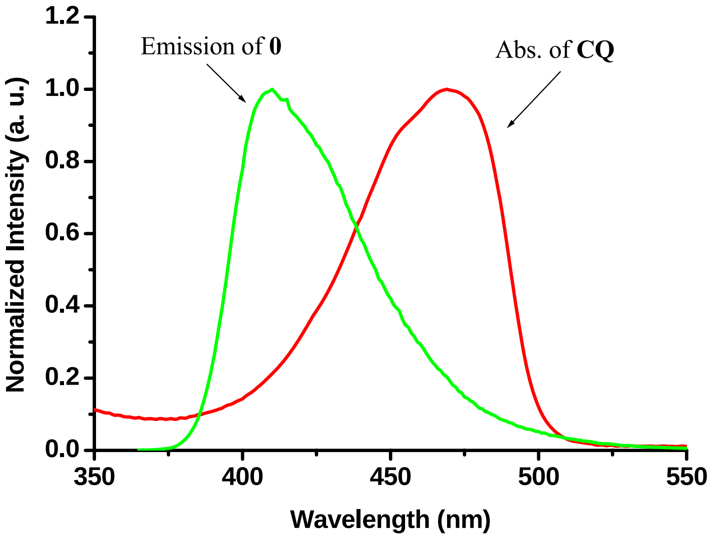


Figure S.1: Normalised emission and absorption spectra of **0** and **CQ** in acetonitrile.

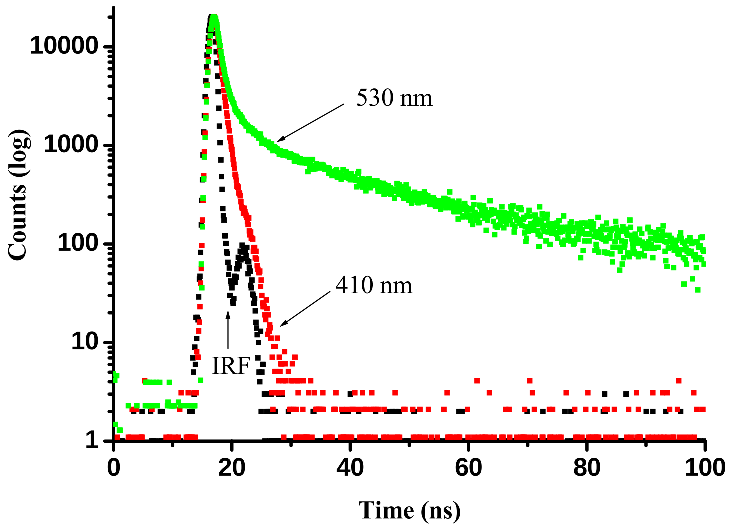


Figure S.2: Fluorescence decays of compound **2** in acetonitrile collected at 410 nm and 530 nm, respectively.

Two-photon Absorption Cross-Section Measurements.

A relative two-photon induced fluorescence method[6, 7] was employed to measure the two-photon absorption cross-sections, ***δ***, with a femtosecond pulsed laser as excitation source. Using a reference chromophore (*r*) for the two-photon cross-section measurement, the value of ***δ*** for a sample (*s*) is given by:

$$\delta_S = \frac{S_S \Phi_r \eta_r C_r}{S_r \Phi_S \eta_S C_S} . \delta_r \qquad (3)$$

where ***S*** is the detected two-photon induced fluorescence integral area, ***C*** the concentration of the chromophore, and ***Φ*** is the fluorescence quantum yield of chromophore. ***η*** is the collection efficiency of the experimental set-up and accounts for the wavelength dependence of the detectors and optics as well as the difference in refractive indices between the solvents in which the reference and sample compounds are dissolved.[8, 9] The measurements were conducted in a regime where the fluorescence signal showed a quadratic dependence on the intensity of the excitation beam, as expected for two-photon–induced emission.

For the femtosecond-pulse experiment, the two-photon cross sections were measured using a Ti: Sapphire laser as the excitation source (Spectra-Physics, Mai Tai : pulse duration: 100 fs; repetition rate: 80 MHz; wavelength range: 690-1020 nm). The reference standard used is Coumarin 480 in methanol (with $\boldsymbol{\delta}$ = 160 GM, at 781 nm)[9]. The collection of the two-photon–induced fluorescence signal was performed at the same detection wavelength for coumarin 480 and compounds **0–2** (i.e. : 460 nm). The concentration of the solutions was in the range of $3–4 \times 10^{-4}$ M for compounds **0–2**. The laser intensity was in the range of $0.2\text{-}2 \times 10^9$ W/cm^2. The experimental error on the reported cross section is 15 – 20%.

Laser flash photolysis.

The laser flash photolysis system used for the excited state transient absorption experiments is based on a nanosecond optical parametric oscillator (Sunlite, Continuum) pumped by a Nd: YAG laser (Powerlite 9010, Continuum) that generates narrow-band radiations in the VIS and the near-IR spectral region. After frequency doubling, the wavelength is tuneable from 266 to 1064 nm; the energy is ca. 50 mJ at 532 nm. The analysing system (LP900, Edinburgh Instruments) is equipped with a 450-W pulsed Xe arc lamp, a Czerny-Turner monochromator, and a fast photomultiplier. The experiments were done in degassed acetonitrile (Spectroscopic grade; Aldrich) on samples having an optical density of 0.5 at the excitation wavelength (266 nm).

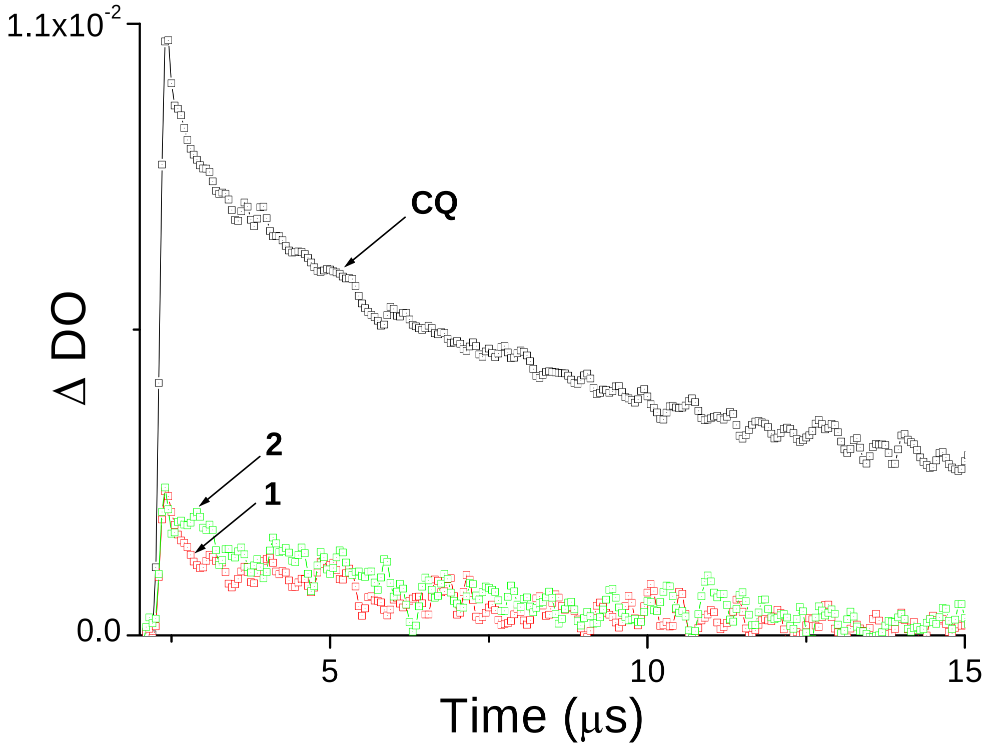


Figure S.3. Transient decay recorded at 800 nm for compounds **1**, **2** and **CQ** in oxygen-free acetonitrile (λ_{exci} = 266 nm)

Two-photon polymerization.

The resin consisted in a diacrylate monomer, SR344 from Sartomer. The mass ratios of the photoinitiator (**2**) and the coinitiator (N-methyl diethanolamine) were 0.5 % and 3 % respectively. The formulation was poured onto a glass slide and laminated with a cover glass. The same laser as used for the TPA cross section measurements was focused through a lens (*f* = 5 cm). The average power used was 1.2 mW. The sample was placed on an X-step motorised stage controlled by a computer. The two-photon polymerized lines were recorded and dimensioned with a transmitted light microscope.

Point-by-point exposure experiments[10-12] are performed with formulations containing the same monomer and coinitiator (3 % wt). In both cases, the concentration of compound **0** or compound **2** is 4×10^{-3} mol. L^{-1}. The average power of incident light is fixed at 0.7 mW. Upon increasing the time exposure (τ_{exp}) from 3 s to 120 s, voxels of increasing dimensions are polymerized. Averages of measurements are obtained from five voxels per time exposure (figure S.4). Assuming that the incident intensity presents a gaussian profile in the focal plan and that the diffusion lengths of the reactive species are negligible in comparison with the size of the photopolymerized structures, the dependence of the voxel radius on the irradiation time exposure, for a fixed incident power can be expressed as follows :

$$r = \omega_0 \sqrt{\ln(\frac{\tau}{\tau_{\min}})}$$

In this equation, ω_0 denotes the beam waist (600 µm) and $\tau_{\min}$ corresponds to the minimum exposure duration above which polymerization occurs. The least square analysis of experimental data yields values for $\tau_{\min}$ of 1.46 ± 0.12 s for compound **0** and of 0.25 ±0.06 s for compound **2**. Hence the ratio of $\tau_{\min}$ leads to the ratio polymerization thresholds[11].

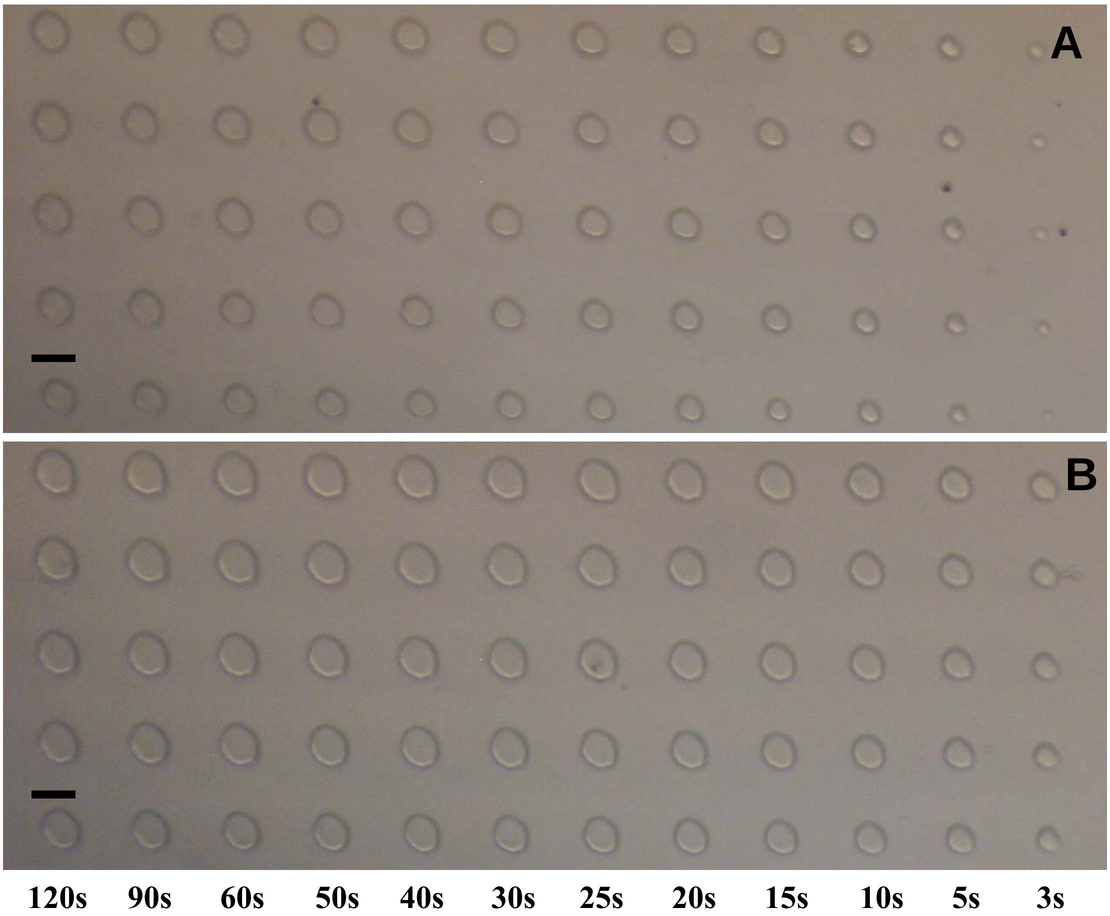


Figure S.4. Two-photon polymerization voxels obtained with point-by-point exposures at various exposure times (**A** : compound **0** , **B** : compound **2**). Scale bar : 40 µm

References

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