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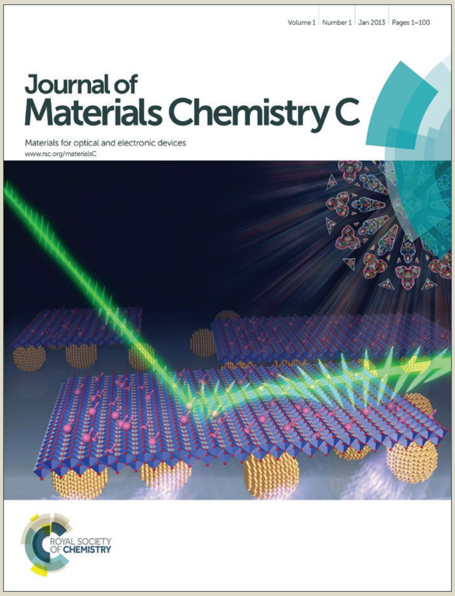

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ARTICLE

π-Expanded 1,3-Diketones – Synthesis, Optical Properties and Application in Two-Photon Polymerization

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Four π-expanded α,β-unsaturated 1,3-diketones have been prepared *via* attaching strong electron-donating and electron-withdrawing groups at positions 9 and 10 of the anthracene scaffold. The strategic incorporation of $(C_{12}H_{25})_2N$ groups at the periphery of these D-π-A molecules resulted in dyes with excellent solubility in most organic solvents. These non-planar diketones possess very broad absorption of light and negligible fluorescence. The two-photon absorption cross-section was measured *via* Z-scan as well as by two-photon excited fluorescence. The results clearly confirm that, in the case of compounds possessing such small fluorescence quantum yields, the Z-scan was a more reliable approach. Depending on the chemical structure, these compounds exhibited two-photon absorption cross-sections (σ_2) up to 2500 GM at 725 nm. For the first time an α,β-unsaturated ketone derived from a proton sponge has been synthesized and was shown to possess optical features distinct from its simpler analogs, such as weak emission. All studied ketones possessed two-photon absorption cross-sections ~200 GM at wavelength of two-photon polymerization (i. e. 800 nm) and broad fabrication windows have been achieved using all these dyes as photoinitiators.

Introduction

Although the first example of multi-photon photopolymerization (MPP) was reported in 1965 by Pao and Rentzepis,[1] it was the pivotal work by the Kawata group in 1997[2] that brought widespread attention to this technique.[3-13] The development of novel monomers[14] and photo-initiators for MPP[15-25] have been the subject of intense investigation.[26-29] Much of the research in this field has followed the pioneering work on classical photoinitiators for polymer synthesis by the Fouassier group.[30-39] Several classes of compounds have been investigated in recent years, including α,β-unsaturated ketones,[22,23,40] acylphosphine oxides[25] and thioxanthones.[41] Construction of the scaffolds for tissue engineering and cell growth,[42-45] micromechanical devices,[46-49] and nanophotonic and metamaterial structures[50-52] have been the driving forces towards the rapid development of this technique. Both a large two-photon absorption cross-section and a high yield of photo-initiation are critical for the overall performance of a given photoinitiator. Another important, but often overlooked, factor is the solubility of the photoinitiator in the monomer. Needless to say, liquid photoinitiators are highly sought since solid ones tend to dissolve poorly and slowly in monomers. Ketones are excellent choices, since the carbonyl group is a strong electron-withdrawing moiety which is necessary to obtain large two-photon absorption cross-sections and it is also a known functionality responsible for Norrish type 1 photoinitiators.[53-55] The α,β-unsaturated ketones possessing electron-donating groups have been the focus of recent studies since they are useful in such diverse areas such as: two-photon excited photodynamic therapy,[56,57] two-photon fluorescence microscopy,[58] emission in the solid-state[59] and photoinitiators of polymerization.[18,60] However, only very recently have their photophysical properties been examined in detail.[61-63] While benzene is the classical central π-system used in the construction of push-pull dyes,[56,64] investigations of larger building blocks such as anthracene, especially anthracene-derived α,β-unsaturated ketones, are virtually unknown. Based on the breakthrough studies by Fouassier and Lalevée, we opted to use 1,3-diketones rather than simple ketones as the electron-withdrawing moiety.[35,40,65] 1,3-Diketone is a strong electron-withdrawing group.[66,67] Its presence results in the decrease in fluorescence quantum yield which is a prerequisite for a compound to be an initiator of photopolymerization. The presence of a 1,3-diketone also broadens the absorption spectrum,[35] which, in principle, should also broaden the two-photon absorption spectrum, increasing the chance of achieving MPP using a suitable laser. We reasoned that the

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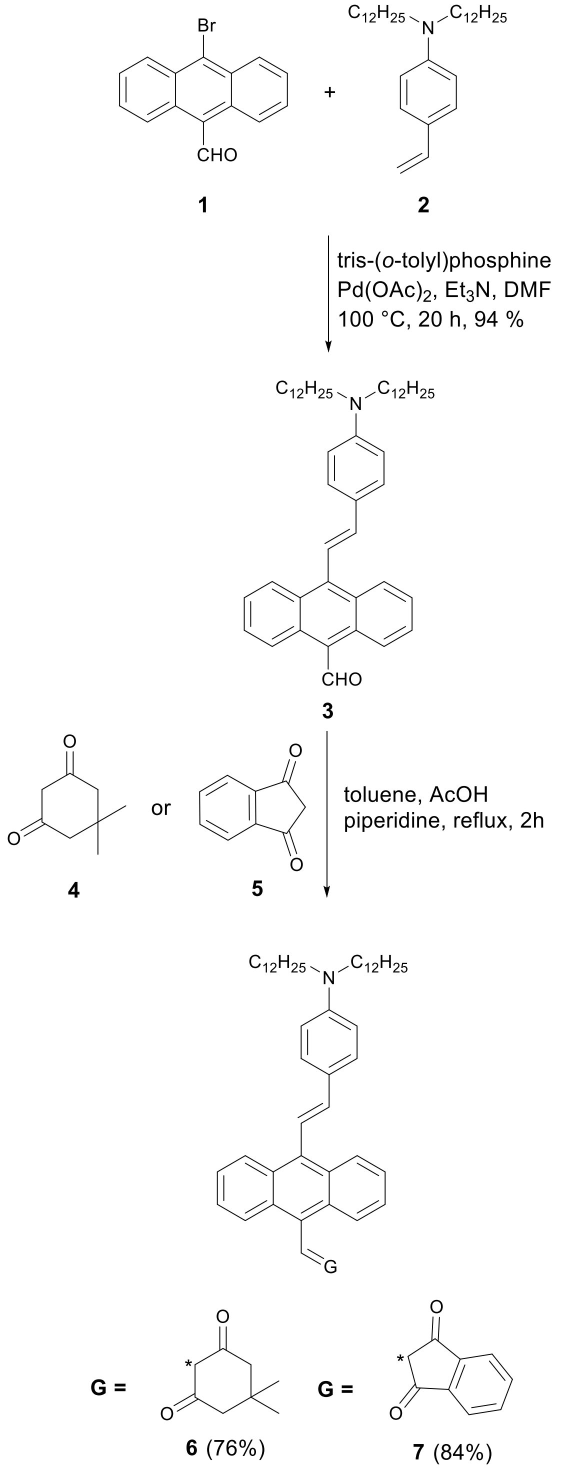
combination of D-π-A architecture with 1,3-diketone as acceptor unit and large π-system should lead to notable 2Photon Absorption-cross section (σ_2) at the wavelength of interest.

Results and Discussion

Design and synthesis. Based on our previous results, based on the efficiency of α,β-unsaturated ketones in MPP,[18,19] we designed the next generation of compounds.

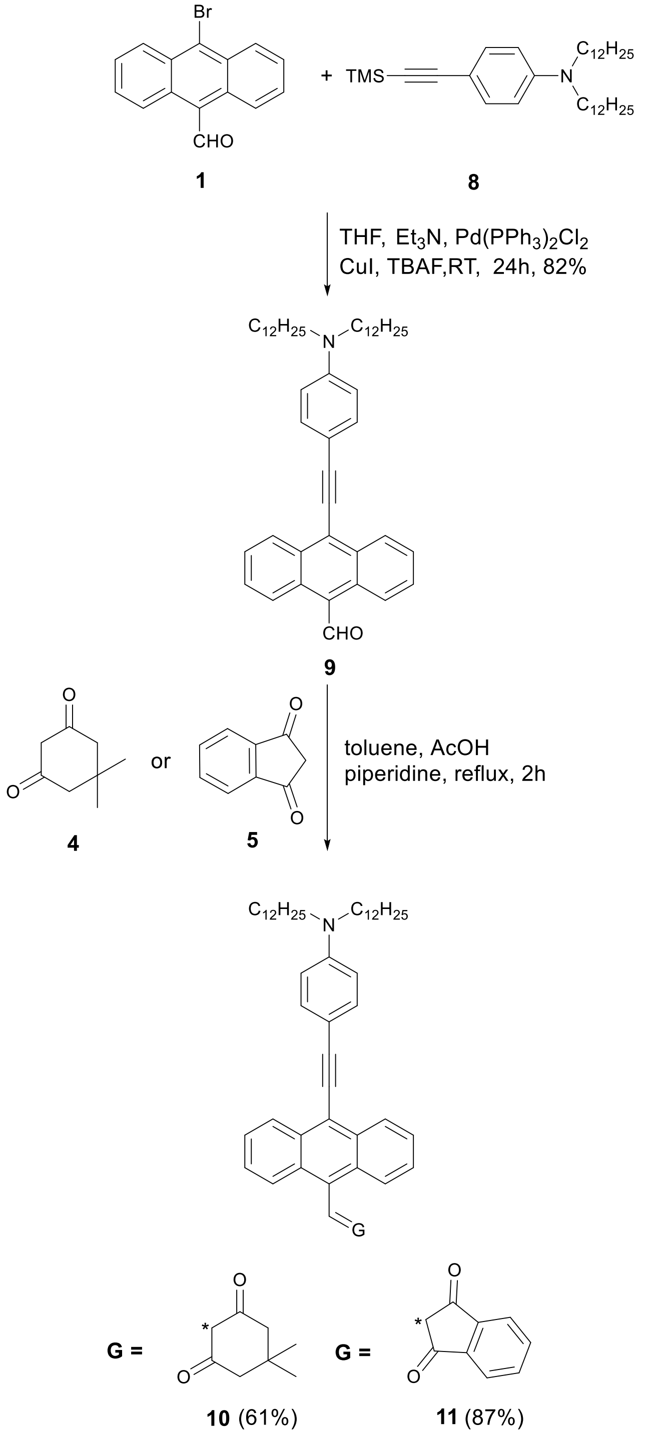


Scheme 1

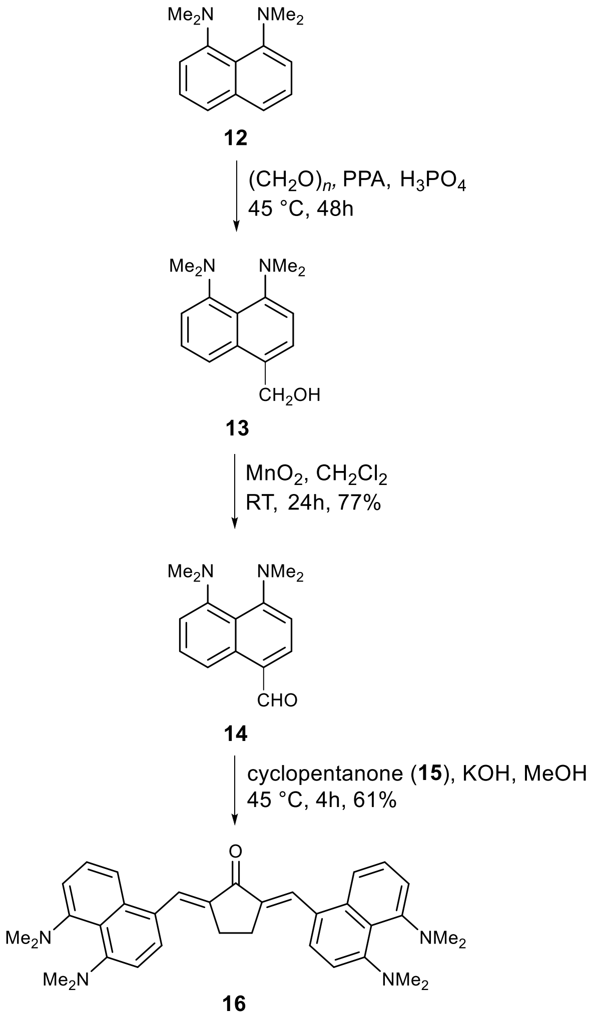
The crucial part was to maximize the chance that the two-photon absorption cross-section (σ_2) would be at the wavelength of interest, i.e. ~800 nm. At the same time, we sought to introduce more polarized chromophores containing stronger electron acceptors, i.e., 1,3-diketones.

The general structure of these new dyes was based on anthracene as the π-linker connected with an electron donor, dialkylaminobenzene, and an electron acceptor, 1,3-diketone. Two different types of diketones, i.e., indanedione and dimedone (5,5-dimethylcyclohexane-1,3-dione) were chosen as acceptors. Being aware of the work of Blanchard-Desce,[68] which clearly showed that linkers with carbon–carbon double bonds or triple bonds had different effects in mediating the charge transfer, we chose to use both these linkers. Since solubility is critical for overall performance of the sensitizer, we opted to use long alkyl chains, which have been proven to ensure proper solubility.[18,19]

The synthesis started from aldehyde **1**, which was prepared from 9,10-dibromoanthracene by means of a metal–halogen exchange reaction (Scheme 1).[69] Compound **3** was synthesized *via* Heck reaction of alkene **2** with 9-bromo-10-formylanthracene (**1**). Since aldehyde **3** is both sterically hindered and relatively electron-rich, we anticipated that its reactivity in the Knoevenagel condensation would be diminished. In order to achieve the best yield, we performed an optimization study using aldehyde (**3**) and dimedone (**4**) as model substrates. The majority of the reported reaction conditions that we utilized (acetic acid in methanol,[70] *L*-proline in methanol,[71] piperidine in metanol,[39] potassium hydroxide in 1,4-dioxane,[72] acetic acid/triethylamine in ethanol)[73] led to the formation of expected product **6**, but only in low yield. The highest yield was achieved by using piperidine and acetic acid in toluene at reflux conditions for 2 h. The same conditions were used to carry out Knoevenagel condensation with ketone **5**, leading to dye **7** in 84% yield (Scheme 1). An analogous strategy was employed in the synthesis of ketones **10** and **11** (Scheme 2). Aldehyde **1** was condensed with alkyne **8** *via* Sila-Sonogashira reaction to lead to aldehyde **9**. Knoevenagel reaction of aldehyde **9** with ketones **4** and **5** gave corresponding dyes **10** and **11** in 61% and 87% yields, respectively (Scheme 2). Finally, we ventured to investigate the influence of a different type of electron-donating moiety, i.e., a proton sponge, on the linear and non-linear optical properties of α,β-unsaturated ketones as well as the photoinitiating ability in MPP. Pozarsky and co-workers developed the synthesis of aldehyde **14** *via* two alternative routes. In the first route they synthesized aldehyde **14** with 7% yield[74] and in the second strategy, they synthesized intermediate **13** following oxidation by TiO_2 to afford aldehyde **14** in moderate yields.[75] The yield of aldehyde **14** improved compared to Pozarsky's procedure *via* oxidation of **13** using MnO_2 (overall 71% yield, Scheme 3). Finally, aldehyde **14** was condensed with cyclopentanone **15** to yield α,β-unsaturated ketone **16** in 61% yield under basic conditions (Scheme 3).



Scheme 2



Scheme 3

Linear optical properties. The optical properties of the five ketones were investigated in DCM (Table 1, Figs. 1-2). The absorption maxima of ketones **6**, **7**, **10** and **11** are in the range 500-600 nm (Table 1). Interestingly, in the case of all these compounds, the absorption was very broad but there were no obvious low-energy intramolecular charge transfer (ICT) absorption bands, as observed by Lavalée and co-workers at 620 nm for analogous of 2-(4-(dimethylamino)benzylidene-indene-1,3-dione.[35] The difference in conformation imparted by a larger dihedral angle due to the substitution of a benzene ring with an anthracene ring is most probably responsible for this difference. The deviation from planarity for 1,3-diketones **6**, **7**, **10** and **11** was also reflected in their low molar absorption coefficients (~10000-20000 M^{-1} cm^{-1}), much lower than that previously reported for α,β-unsaturated-1,3-diketones.[35,63]

For compounds **6/7** and **10/11**, one can observe a correlation between the size of the alicyclic ring and the position of the absorption band (Fig. 1, Table 1). The absorption maxima of **6** and **10** (cyclohexane-1,3-dione ring) were significantly blue-shifted (~30 nm) relative to **7** and **11** (indene-1,3-dione moiety). The six-membered ring must be even more tilted out-of-plane, as compared to the five-membered ring. The shape of

Table 1. Optical properties for compounds **6**, **7**, **10**, **11** and **16** in DCM.

Cmpd	λ_{abs} (nm)	ε (M^{-1} cm^{-1})	λ_{em} (nm)	Φ_{fl} (%)	Δν (cm^{-1})	$2\lambda_{1PA}$ [nm]	λ_{TPA}^{max} [nm] Z-scan	σ_2^{max} [GM] Z-scan	λ_{TPA}^{max} [nm] 2PEF	σ_2^{max} [GM] 2PEF
6	435 511	7100	572	0.020	2100	870 1020	725	700	970	<8000
7	395 542	12300	629	0.010	4500	790 1080	725	970	710	<2000
10	470 521	10700	531	1.010	300	940 1042	725	1000	710	200
11	439 561	18500	761 820	<0.001	4700	880 1120	725	2500	nd	nd
16	362 502	14900	611	0.110	3500	724 1004	725	600	820	580

nd – not determined due to extremely weak emission

absorption for ketones **6** and **10** is different than that of **7** and **11**, namely both bands located in the visible region have similar intensity. Moreover there is almost no bathochromic shift, while proceeding from a more conjugated dye **10** with C-C triple bond as a linker to compound **6** possessing C-C double bond as a linker. The presence of the latter one in dyes **6** and **7** has to cause significant distortion from planarity due to steric interactions between anthracene hydrogens and one of hydrogens attached to C-C double bond. An analogous red-shift while moving from dye **7** to compound **11** is much more noticeable (~20 nm).

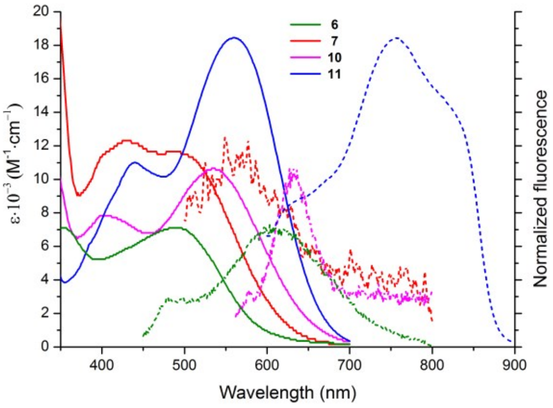


Fig. 1. Absorption (solid lines) and emission (dotted lines) spectra of compounds **6** (green), **7** (red), **10** (magenta) and **11** (blue) in DCM.

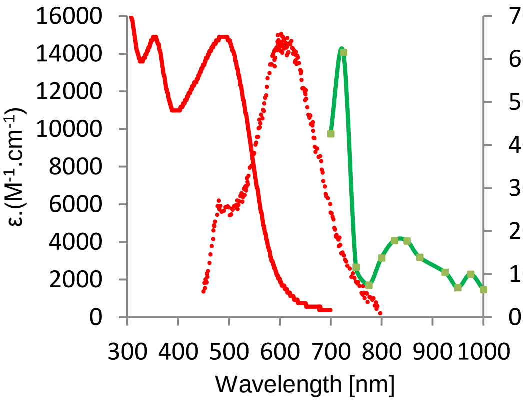


Fig. 2. Absorption, emission, and two-photon absorption (green line) spectra of dye **16** in DCM.

Although all these 1,3-diketones emitted red light, their fluorescence quantum yields were found to be very low (below 0.1 %). For ketone **11**, we observed broad fluorescence peaks at 760 and 820 nm (Table 1).

Compound **16** possesses different structure and is more related to 2,5-bis(4-diethylamino)benzylidene)cyclopentanone[62] and 2,5-bis((6-(didodecylamino)benzofuran-2-yl)methylene)cyclopentanone.[63] Its optical properties are, however, markedly different from those of these two bis(arylidene)cyclopentanones. The comparison of linear optical properties of ketone **16** with 2,5-bis(4-diethylamino)benzylidene)cyclopentanone clearly showed that there was only small red-shift of absorption (520 nm vs. 480 nm), but there was a strong bathochromic shift of emission (610 nm versus 550 nm). The rationale behind this observation clearly originates from switching of geometry (non-planar in the ground state and planar in the excited state). The fluorescence maximum is comparable with analogous ketone possessing two 6-dialkylaminobenzofurylidene groups as electron donors.[63] At the same time, the Φ_{fl} values obtained for dye **16** were much lower than any other bis(arylidene)cyclopentanone published so far (0.11 % in CHCl$_3$ vs. 26% for 2,5-bis(4-

diethylamino)benzylidene)cyclopentanone[62] and 19% for 2,5-bis((6-(didodecylamino)benzofuran-2-yl)methylene)cyclopentanone).[63] The Stokes shift for compound **16** in DCM was comparable to values obtained for 2,5-bis(4-diethylamino)benzylidene)cyclopentanone and 2,6-bis(4-diethylamino)benzylidene)cyclohexanone by Wu and co-workers.[62]

To validate conclusions about the role of steric interaction between anthracene hydrogen and one of the hydrogens attached to C=C double bond, computational calculations with full geometry optimization were carried out using DFT B3LYP/6-31G(d,p) method implemented in the Gaussian09 package.[76] In these calculations molecules **6**, **7**, **10** and **11** were truncated by simple analogues **6'**, **7'**, **10'** and **11'**, wherein the -N($C_{12}H_{25}$)$_2$ groups were replaced by -N(CH_3)$_2$ groups. Optimization of molecular structures were confirmed by the positive values of all frequencies from their molecular vibrations. In addition, the energies and oscillator strengths for electronic excitations from the ground state S_0 to the electronic excited states Si (i =1-5) have been calculated using TD DFT B3LYP /6-31G(d,p) method. The coordinates of the atoms of the optimized **6'**, **7'**, **10'** and **11'** molecules and some other results of calculations can be seen in Tab.S1 and S2 in the ESI. According to our calculations the geometries of compounds **6'** and **7'** (with link by C=C) differ from the geometries of compounds **10'** and **11'** (with link C≡C) by lacking coplanarity between the planes of the anthracene and the dimethylaniline rings (see Fig. 3 and Tab.S1). At an angle of 57 degrees between these two planes in **6'** and **7'**, the smallest distances between the H atom of anthracene and H of the C=C bridge are 2.152 and 2.139 Å (compared to the co-planar structures whose distance would be approx. 0.97 Å).

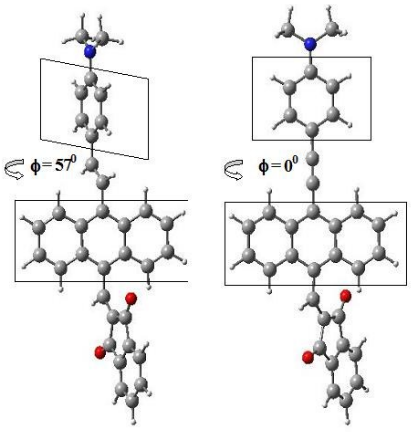


Fig. 3. Relative orientation of anthracene and dimethylaniline planes in dependence on linkage between them: (C = C (on the left) and C ≡ C) for the optimized molecules **7'** and **11'**.

The relationship between the electronic spectra and structure of compounds **6'**, **7'**, **10'** and **11'** can be summarized as follows: According to our calculations (for all four molecules) the excitation $S_0 \rightarrow S_1$ is described as a transition from HOMO to LUMO orbitals. The shapes of these orbitals are shown in Table S2. The HOMO orbitals are composed from the orbitals localized on anthracene and donor, while LUMO orbitals from the orbitals localized on anthracene and acceptor. Therefore: (1) the character of $S_0 \rightarrow S_1$ transition is mixed – locally excited and charge-transfer, (2) the coplanarity or the lack of it between anthracene and donor group has an impact on the spatial shape of the HOMO orbital and (3) in contrast, the type of linkage between the donor and the anthracene has little influence on the shape of the LUMO orbital.

According to our calculations the change in the type of linkage from C=C to C≡C is associated with: (1) a red shift of the absorption band of ~300 and ~500 cm^{-1} in dependence on the type of acceptor group and with the increase of the oscillator strength of 1.3 times. These values are indeed somewhat smaller than those observed experimentally, but describe the same direction of change.

Two-photon absorption. Two-photon absorption cross-sections were measured for compounds **6**, **7**, **10**, **11** and **16** in the range 700-1000 nm using two methods (Table 1). Z-scan measurements were chosen as a primary tool. Z-scan measurements showed, according to expectations, a very strong two-photon response in this family of compounds (Table 1), which originated from the combined effects of a large π-system and the placement of strong electron-donating groups and very strong electron-withdrawing groups within the push-pull systems. In the case of compounds **6**, **7**, **10** and **11** maxima of 2PA (~725 nm in all cases) corresponds to no clear transitions at the 1PA spectrum. This wavelength is relatively close to the onset of one-photon absorption, so one cannot exclude some contribution of a sequential process consisting in one-photon absorption followed by excited state absorption. The contribution from a three-photon process, which is two-photon absorption followed by an excited state absorption, is also possible. The values for dyes bearing a carbon-carbon triple bond were higher than for their analogs bearing the ethylene linker. Dyes **7** and **11,** bearing stronger electron-withdrawing indene-1,3-dione moiety, possessed higher σ_2 than their analogs **6** and **10** bearing six-membered ring.

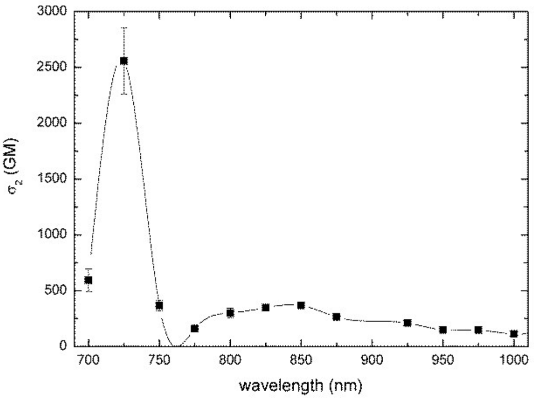


Fig. 4. Two-photon absorption spectrum of dye **11** measured by Z-scan technique.

In the two-photon spectra of ketones **6**, **7**, **10** and **11** both g→c and g→e transitions should be observed since these molecules are not centrosymmetrical.[77-79] Strikingly, although indeed two bands are always present in their location it does not strictly correspond to half energies of transitions present in the linear spectra.

The maximum value of 2PA cross-section for ketone **16** was appreciable (600 GM) and identical to what was determined for analogous bis(4-dimethylaminobenzylidene)cyclopentanone.[62] The same value can be attributed to interplay between 1,8-bis(dimethylamino)naphthalene being a weaker electron-donor than 4-dimethylaminophenyl, and the overall expansion of the π-system. For bis(4-dimethylaminobenzylidene)cyclopentanone Wu and co-workers confirmed, via fluorescence anisotropy measurements, that the shoulder peak at 425 nm is not of vibronic nature but it comes from an S_0-S_2 transition, which corresponds to symmetry-allowed transition in 2PA.[62] In the case of ketone **16**, S_0-S_2 transition is located at 362 nm, which corresponds to observed maxima at 2PA spectrum at 725 nm. On the other hand, in contrast to what has been observed earlier[62] there is no clear S_0-S_1 transition at 2PA spectrum (which should be visible at ~1000 nm). Instead, a weak band at 830 nm is observed.

It is important to emphasize that all studied dyes have very similar σ_2 (200±50 GM) at wavelength used for two-photon excited polymerization (i.e 800 nm, Figs. 2 and 4 and ESI). Analogous dipolar anthracene push-pull dyes bearing the dialkylaminophenylethylene substituent as the electron-donor and 4-cyanophenylethylyne as the electron-acceptor had lower two-photon absorption cross-sections (250 GM).[80] In contrast, the analogous quadrupolar compound bearing two diarylaminophenylethynyl substituents displayed a cross-section value of 550 GM.[81]

2PA measurements using 2PEF were also performed to investigate how reliable 2PEF can be for compounds possessing such low fluorescence quantum yields. 2PEF is a relative method involving the division of the 2PEF from the dyes with the 2PEF of a reference. Therefore as the fluorescence of the probe goes towards 0, errors become large. Also, the value of the quantum yield, small or large, of the dyes is used for the calculations of the 2PA measurements.. Small errors in the absolute values of the quantum yield can lead to large changes of the measured 2PA. In this work it is seen that the 2PEF measurements are reliable for the samples with such low quantum yield. However, it generally overestimates the 2PA cross sections. Therefore the z scan method is reliable and thus the method of choice.

Polymerization. In order to test whether the investigated photoinitiators were suitable for one-photon polymerization, drop-cast films of each composite were placed under a wide-spectrum UV lamp. All samples fully polymerized after a few minutes of exposure.

To evaluate the two-photon initiation potential of the new composites, we studied several parameters related to the response of the composite material with respect to the applied laser power (Fig. 5). (i) The polymerization threshold is the lowest laser power required to have some polymerized structure in the substrate after sample development. This process is characterized by pieces of shapeless polymer, without a well-defined geometry. (ii) The structuring threshold is the lowest laser power required to make complete structures without deformations. (iii) The burning threshold is defined as the laser power at which ablation starts and the material burns. (iv)The fabrication window (FW) is defined as the power difference between the polymerization threshold and the burning threshold. A large FW is desirable, as it allows the use of higher power lasers, allowing fabrication at faster and manufacturing-level scales. As a reference material (R), we used (4,4′-bis(diethylamino) benzophenone)), a commercially available photo-initiator used often in MPP.

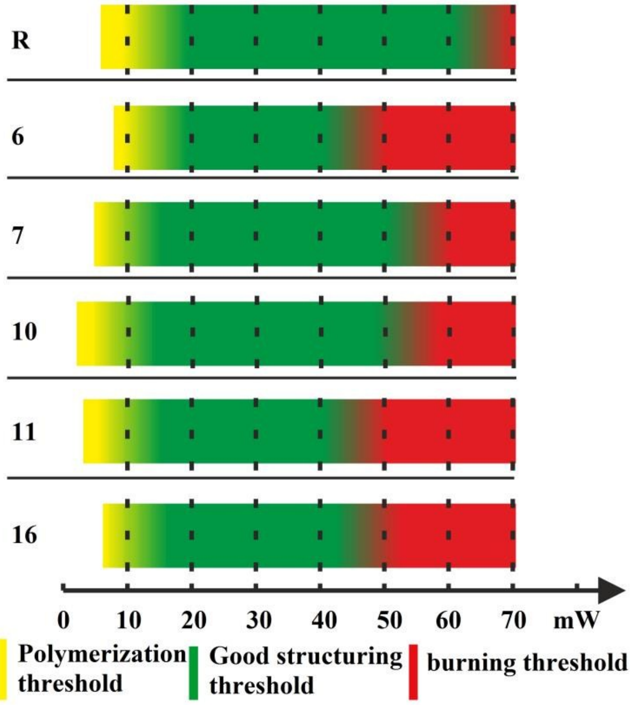


Fig. 5. The polymerization (yellow), good structuring (green), and burning (red) thresholds of the five materials prepared in this study. The reference material (R) is 4,4′-bis(diethylamino) benzophenone.

The polymerization parameters were found by structuring the different compounds using a series of increasing laser powers. The results are summarized in Figure 5. All materials possessed broad and well-defined FWs, comparable to the reference photoinitiator.

Figure 6a shows an example of 3D free-standing, hollow pyramids fabricated by employing the photopolymer with photoinitiator **10** and increasing laser power (left to right). The three pyramids, prepared with 15, 25 and 40 mW laser power, were complete and well defined. As the average laser power increased the areas outside the pattern started forming and eventually, at laser power of 50 mW, the structures burned and collapsed. Figure 6b shows in magnification one of the pyramids which was fabricated using 30 mW average laser power. In general, the investigated PIs were comparable to the reference material.

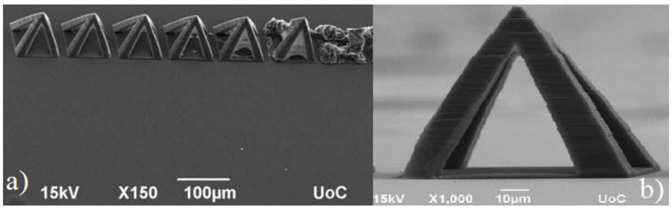


Fig. 6. a) A SEM micrographs showing an array of micropyramids fabricated using the **10** photoinitiator under conditions of increasing average laser power. b) A hollow pyramid fabricated using the **10** photoinitiator at 30 mW average laser power.

Experimental Section

Materials and Synthesis. All commercially available compounds were used as received. All solvents were dried and distilled prior to use. Transformation of oxygen sensitive compounds were performed under argon atmosphere. The reaction progress was monitored by means of thin layer chromatography (TLC) which was performed on aluminium sheets, coated with silica gel 60 F254 (Merck) or aluminium oxide 60 F254 (neutral Merck) with detection by a UV lamp. Product purification was done by means of column chromatography with silica flash P 60 (40–63 µm, SiliCycle) or aluminium oxide 90 (neutral, 70– 230 mesh, Merck), dry column vacuum chromatography (DCVC)[82] with silica (MN-Kieselgel P/UV254) or Aluminum oxide (MNAluminumoxid G). Identity and purity of the prepared compounds were proved by ^{1}H NMR and ^{13}C NMR (Varian 500/200 MHz). High resolution mass spectra (ESI HRMS) were obtained on MaldiSYNAPT G2-S HDMS/GCT Premier, Waters. 9-Bromo-10-anthracenecarboxaldehyde (**1**),[69] N,N-didodecyl-4-vinylaniline (**2**),[41] and N,N-didodecyl-4-((trimethylsilyl)ethynyl)aniline (**8**)[83] were obtained by the reported methods.

(E)-10-(4-(Didodecylamino)styryl)anthracene-9-carbaldehyde (3). In an oven-dried Schlenk tube under continuous argon flow, compound **1** (566 mg, 2 mmol), **2** (910 mg, 2 mmol), Pd(OAc)$_2$ (15 mg, 0.066 mmol), tris-(o-tolyl)phosphine (40.2 mg, 0.134 mmol), Et$_3$N (2 mL, 14.3 mmol) and finally anhydrous DMF (8 mL) were mixed. The Schlenk tube was sealed and heated at 100 °C for 20 h. The reaction mixture was then poured into 200 mL of water and extracted using DCM (100 mL × 3 times), dried over Na$_2$SO$_4$ and concentrated under vacuum. Purification via DCVC (silica, DCM/hexanes 0:100 to 5:95) afforded the product as a red viscous oil with 94% yield. R$_f$ = 0.6 (DCM/hexanes 1:2); ^{1}H NMR (CDCl$_3$, 500 MHz) δ 11.5 (s, 1H), 9.02 (d, *J* = 8.5Hz, 2H), 8.5 (d, *J* = 1.5 Hz, 2H), 7.69-7.65 (m, 4H), 7.54-7.49 (m, 4H), 6.85 (d, *J* = 16.5 Hz, 1H), 6.72 (d, *J* = 16.5 Hz, 2H), 3.35 (t, 4H), 1.64-1.62 (m, 4H), 1.30-1.22 (m, 36H), 0.89 (t, 6H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 192.6, 133.5, 133.4 (2 signals), 131.7, 131.2, 129.0, 128.9, 128.1, 128.0, 126.1 (2 signals), 123.7, 111.4 (2 signals), 111.3 (2 signals), 51.0, 31.9, 29.6 (2 signals), 29.5, 29.4 (2 signals), 29.3, 27.2, 27.1, 22.6, 14.1; HRMS (ESI):m/z ([M+H]$^+$) $C_{47}H_{65}NO$: calculated 659.5066; found: 659.5075.

General procedure for the synthesis of α,β-unsaturated 1,3-diketones 6, 7, 10 and 11. Under the flow of argon the following reagents were added to toluene (5 mL): aldehydes **3** or **9** (0.5 mmol), the corresponding cyclic diketone (0.5 mmol), piperidine (42.5 mg, 0.5 mmol) and glacial acetic acid (30 mg, 0.5 mmol). After refluxing for 2 h, the reaction mixture was cooled, diluted with 50 mL of Et$_2$O and washed with 10 mL saturated NaHCO$_3$ followed by 10 mL of water. The organic phase was dried (MgSO$_4$) and the solvent removed by rotary evaporation.

(E)-2-((10-(4-(Didodecylamino)styryl)anthracen-9-yl)methylene)-5,5-dimethylcyclohexane-1,3-dione (6). Purification via DCVC (silica, DCM/hexanes 1:5 to 1:1) afforded the product as a red gel with 76% yield. R$_f$ = 0.6 (DCM/hexanes 2:1); ^{1}H NMR (CDCl$_3$, 500 MHz) δ 8.92 (s, 1H), 8.44 (d, *J* = 8.5Hz, 2H), 7.82 (dd, *J*$_1$ = 1.5 Hz, *J*$_2$ = 1.5 Hz, 2H), 7.68 (d, *J* = 16.5Hz, 1H), 7.44-7.40 (m, 4H), 6.85 (d, *J* = 16.5 Hz, 1H), 6.71 (d, *J* = 16.5 Hz, 2H), 3.33 (t, *J* = 14.5 Hz, 4H), 2.78 (s, 2H), 2.50 (s, 2H), 1.62 (m, 4H), 1.34-1.27 (m, 36 H), 1.27 (s, 6H), 0.89 (t, *J* = 13.5 Hz, 6H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 197.4, 195.5, 149.5, 148.1, 138.1, 136.8, 136.6, 129.2, 128.6, 128.2, 127.9, 127.3, 126.0, 125.3, 124.9, 124.3, 119.1, 111.7, 53.7, 52.9, 51.1, 31.9, 30.0, 29.7, 29.6, 29.5, 29.3, 28.7, 27.3, 27.1, 22.6, 14.1 HRMS (ESI):m/z ([M+H]$^+$) $C_{55}H_{75}NO_2$: calculated 781.5798; found: 781.5823. Anal. Calcd for $C_{55}H_{75}NO_2$: C, 84.45; H, 9.66; N, 1.79, Found: C, 84.48; H, 9.80; N, 1.69.

(E)-2-((10-(4-(Didodecylamino)styryl)anthracen-9-yl)methylene)-1H-indene-1,3(2H)-dione (7). Purification via DCVC (silica, acetone/hexanes 1:50 to 1:30) afforded the product as a red viscous oil with 84% yield. R$_f$ = 0.6 (acetone/hexanes 1:20); ^{1}H NMR (CDCl3, 500 MHz) δ 8.95 (s, 1H), 8.50 (d, *J* = 8.5Hz, 2H), 8.14 (d, *J* = 7.5 Hz, 1H), 8.03 (d, *J* = 7.5Hz, 2H), 7.88-7.78 (m, 4H), 7.73 (d, *J* = 16.5 Hz, 1H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.50-7.45 (m, 3H), 6.90 (d, *J* = 16.5Hz, 1H), 6.73 (d, *J* = 8.5Hz, 2H), 3.35 (t, *J* = 14.5Hz, 4H), 1.65 (m, 4H), 1.31-1.27 (m, 36 H), 0.90 (t, *J* = 13.5Hz, 6H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 189.6, 187.6, 148.4, 142.8, 142.2, 140.9, 138.7, 135.6, 135.4, 130.2, 129.4, 128.1, 127.4, 126.7, 125.9, 125.3, 124.3, 123.6, 123.5, 119.2, 119.1, 51.3, 32.0, 29.8, 29.8, 29.7, 29.6, 29.5, 27.5, 27.4, 27.3, 22.8, 14.2; HRMS (ESI):m/z ([M+H]$^+$) $C_{56}H_{69}NO_2$: calculated 787.5328; found: 787.5341. Anal. Calcd for $C_{56}H_{69}NO_2$: C, 85.34; H, 8.82; N, 1.78, Found: C, 85.33; H, 8.74; N, 1.63.

10-((4-(Didodecylamino)phenyl)ethynyl)anthracene-9-carbaldehyde (9). In an oven-dried Schlenk tube, under continuous argon flow, a mixture of compound **1** (566 mg, 2 mmol), alkyne **8** (1.36 g, 2.60 mmol), PdCl$_2$(PPh$_3$)$_2$ (70 mg, 0.1 mmol), CuI (20 mg, 0.1 mmol) in triethylamine (10 mL) and tetrahydrofuran (10 mL) was flushed with argon for 15 min at room temperature. Tetrabutylammonium fluoride (2.50 mL, 1M in THF, 2.50 mmol) was then added drop wise and the resulting solution was stirred overnight at room temperature. Subsequently, the reaction mixture was extracted with ethyl acetate and water (100 mL each), and the combined organic layers were washed with water and brine and dried over Na$_2$SO$_4$. Purification by DCVC (silica, dichloromethane/hexanes

1:10 to 1:5) gave the desired compound as a red viscous oil (545 mg, 82 %).^{1}H NMR ($CDCl_3$, 500 MHz) δ 11.48 (s, 1H), 9.00 (d, *J* = 8.5Hz, 2H), 8.70 (d, *J* = 8.5 Hz, 2H), 7.70-7.60 (m, 6H), 6.69 (d, *J* = 5.5 Hz, 2H), 3.35 (t, *J* = 14.5 Hz, 4H), 1.64 (m, 4H), 1.34 (m, 36 H), 0.89 (t, *J* = 14.5 Hz, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 192.6, 148.7, 134.1, 133.5, 133.4 (3 signals), 131.7, 131.2, 128.9, 128.0, 126.1, 123.7, 111.3, 108.0, 85.0, 51.0, 31.9, 29.65, 29.6 (3 signals), 29.5, 29.4, 29.3, 27.11, 22.6, 14.1; HRMS (ESI):m/z ($[M+H]^+$) $C_{47}H_{63}NO$: calculated 657.4910; found: 657.4905.

2-((10-((4-(Didodecylamino)phenyl)ethynyl)anthracen-9-yl)methylene)-5,5-dimethylcyclohexane-1,3-dione (10). Purification via DCVC (silica, DCM/hexanes 1:5 to 1:2) afforded the product as a red viscous oil with 61% yield. R_f = 0.6 (DCM/hexanes 1:1); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.87 (s, 1H), 8.72 (d, *J* = 8.5Hz, 2H), 7.81 (d, *J* = 8.5 Hz, 2H), 7.61 (d, *J* = 7.5Hz, 1H), 7.56-7.45 (m, 4H), 6.67 (d, *J* = 6.5 Hz, 2H), 3.33 (t, *J* = 14.5 Hz, 4H), 2.77 (s, 2H), 2.50 (s, 2H), 1.63(m, 4H), 1.34-1.25 (m, 36 H), 1.17 (s, 6H), 0.89 (t, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 197.4, 195.5, 148.8, 148.4, 137.0, 134.1, 133.0, 131.4, 129.1, 128.4, 128.0, 127.2, 126.4, 125.9, 125.3, 121.2, 111.3, 84.6, 53.6, 52.8, 51.0, 31.9, 30.0, 29.7, 29.7, 29.6, 29.5, 29.3, 28.7, 27.2, 27.1, 22.6, 14.1.; HRMS (ESI):m/z ($[M+H]^+$) $C_{55}H_{74}NO_2$: calculated 780.5720; found: 780.5726.

2-((10-((4-(Didodecylamino)phenyl)ethynyl)anthracen-9-yl)methylene)-1H-indene-1,3(2H)-dione (11). Purification via DCVC (silica, acetone/hexanes 1:50 to 1:30) afforded the product as a red viscous oil with 87 % yield. R_f = 0.6 (acetone/hexanes 1:20); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.90 (s, 1H), 8.78 (d, *J* = 8.5Hz, 2H), 8.13 (d, *J* = 7.5 Hz, 2H), 8.02-7.79 (m, 2H), 7.64-7.50 (m, 6H), 6.69 (d, *J* = 8.5 Hz, 2H), 3.35 (t, *J* = 14.5 Hz, 4H), 1.65- 1.61 (m, 4H), 1.35- 1.27 (m, 36 H), 0.90 (t, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 189.7, 187.7, 142.8, 142.2, 140.9, 138.7, 135.6, 135.3, 130.2, 129.4, 128.1, 127.5, 127.4, 126.7, 126.6, 125.9, 125.3, 124.3, 123.6, 123.5, 119.1, 111.8, 51.3, 32.0, 29.8 (2 signals), 29.7, 29.6, 29.54, 29.52, 27.4, 27.3, 22.8, 14.2.; HRMS (ESI):m/z ($[M+H]^+$) $C_{56}H_{67}NO_2$: calculated 785.5172; found: 785.5201.

(4,5-Bis(dimethylamino)naphthalen-1-yl)methanol (13). In a 100 mL round bottom flask, N,N,N',N'-tetramethylnaphthalene-1,8-diamine (**12**, 1.07 g, 5 mmol) and polyphosphoric acid (PPA) (2.5 g) were dissolved with stirring in 70% H_3PO_4 (5 mL). The reaction mixture was heated at 45 °C, paraformaldehyde (375 mg, 12.5 mmol) was added to the solution at 45 °C and the mixture was stirred for 48 h at this temperature until the substrate **12** disappeared (TLC). After the reaction was complete, the mixture was diluted with water (100 mL) and alkalized with 20% NaOH to pH 14. The product was extracted with dichloromethane (4 x 25 mL), the extract was concentrated in vacuum and then crude products was dried. This product was used as is without any further purification to synthesize aldehyde **14**.

4,5-Bis(dimethylamino)-1-naphthaldehyde (14). In a Schlenk tube, filled with argon, compound **13** (6 mmol) and manganese dioxide (MnO_2) (1.74 g, 20 mmol) in 30 mL of dry dichloromethane (DCM) were stirred for 24 h at room temperature until the reaction was completed (TLC analysis). The reaction mixture was filtered through Celite, solvent was concentrated under vacuum and the crude product was purified via DCVC (alumina, DCM/hexanes 1:2 to 1:1) afforded a light yellow product in 77% yield. R_f = 0.5 (DCM /hexanes 1:1). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 10.06 (s, 1H), 8.89 (t, *J* = 8Hz, 1H), 7.71 (d, *J* = 8 Hz, 1H), 7.47 (d, *J* = 16 Hz, 1H), 7.02-6.82 (m, 2H), 2.95 (s, 6H) 2.76 (s, 6H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 191.1, 156.5, 150.9, 149.8, 138.9, 135.9, 128.8, 125.0, 116.9, 112.6, 108.5, 44.4, 43.3.; HRMS (ESI):m/z ($[M+H]^+$) $C_{15}H_{19}N_2O$: calculated 243.1497; found: 243.1501.

(2E,5E)-2,5-Bis((4,5-bis(dimethylamino)naphthalen-1-yl)methylene)cyclopentanone (16). To an argon-filled Schlenk tube, the following reagents were added to methanol (10 mL): aldehyde **14** (121 mg, 1 mmol), cyclopentanone **15** (36 µl, 0.44 mmol) and potassium hydroxide (56 mg, 1 mmol). The solution was heated at 45 °C for 4 h and the reaction mixture was cooled. Solvent was concentrated under vacuum and the crude product was purified by DCVC (alumina, acetone/hexanes 5:95) to afford red gel with 61% yield. R_f = 0.6 (dichloromethane/hexanes 1:1) ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.30 (s, 2H), 7.79 (d, *J* = 8, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.41 (t, *J* = 16.5Hz, 2H), 6.97-6.89 (m, 4H), 3.03 (s, 4H), 2.87 (s, 12H), 2.80 (s, 12H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 206.9, 161.8, 156.5, 151.9, 142.1, 136.3, 130.5, 129.8, 126.2, 116.3, 109.5, 108.7, 97.4, 27.3, 27.1, 22.8, HRMS (ESI):m/z ($[M+H]^+$) $C_{35}H_{40}N_4O$: calculated 532.3202; found: 532.3196.

Photophysics

Linear optical measurements. Steady-state fluorescence measurements were performed on dilute solutions (*ca.* 10^{-6} M, optical density < 0.1) contained in standard 1 cm quartz cuvettes. Compounds were dissolved in dichloromethane unless otherwise noted. Emission spectra were obtained, for each compound, under excitation at the wavelength of 500 nm. Fluorescence quantum yields were measured using carboxyfluorescein dissolved in milliQ water (pH = 9, Φ_{fl} = 0.93) as a standard.

Z-scan measurements. The molecules were dissolved in dichloromethane at a 1.0% (w/w) concentration and the solutions were placed in 1 mm path length optical glass cells. The measurements were carried out in a relative manner, calibrating all the data against Z-scans carried out on a fused silica plate and taking into account the nonlinear signals obtained on a cell containing pure solvent.[84] The tunable excitation was achieved by directing the beam from a Quantronix Integra Ti:Sapphire regenerative amplifier (output wavelength 800 nm, pulse duration 130 fs, repetition rate 1 kHz) into an optical parametric amplifier (OPA, a Quantronix Palitra).

Two-photon excited fluorescence (2PEF) measurements. Dichloromethane (CHROMASOLV®, for HPLC, ≥99.9%), methanol (CHROMASOLV®, for HPLC, ≥99.9), 5-Carboxyfluorescein (99% (HPLC)), Rhodamine B and Rhodamine

6G were purchased from Sigma-Aldrich, Denmark. The samples were dissolved in dichloromethane, Rh B and Rh 6G were dissolved in methanol. The fluorescein was dissolved in a CAPS buffer (N-cyclohexyl-3-aminopropanesulfonic acid) pH 11. Concentrations of the samples and references were determined by a dilution series in a spectrophotometer (Perkin Elmer lambda 35) using quartz cuvettes. Single photon fluorescence emission spectra were measured using a spectrofluorometer (ChronosFD from ISS, Champaign, IL USA). The two photon absorption measurements were performed using a custom built multiphoton excitation spectrofluorometer. In short, the excitation source was a Ti:Sa laser (HPeMaiTai DeepSee, Spectra Physics, Mountain View, CA). The laser power was controlled using motorized halfwave plate together with a polarizer. The laser was focused on the sample using a CFI S Plan Fluor ELWD 60X objective (Nikon). The laser power was monitored by a power meter (PM100D with a S142C head, Thorlabs Sweden AB Goteborg, Sweden). The two photon excited emission was collected through the objective and passed through a Multiphoton-Emitter HC 680/SP (AHF analysentechnik AG, Tuebingen, Germany) to a multimode optical fiber (M200L02S-A, Thorlabs Sweden AB Goteborg, Sweden). The emission was then sent to a monochromator (ARC-SP2155, BFi OPTiLAS, Sweden) and the spectra was then imaged by a cooled CCD camera (PIXIS 400B, Princeton Instruments - New Jersey, USA). A motorized XY stage (Nikon) was used as a sample holder. The laser, laser power, camera and XY stage was controlled using ImageJ[72] and custom scripts. Calculations of the two photon cross-sections were done using custom Matlab code (MathWorks, Natick, USA). The absolute 2-photon absorption cross sections were calculated using a relative fluorescence intensity technique as described previously.[85] Fluorescein in a CAPS buffer, (pH11), Rh 6G and Rh B in methanol were used to reference the system, using as references well characterized spectra.[86] The measurements for the two photon cross-sections were carried out at least five times for the different samples with excitation wavelengths from 700 nm to 1020 nm.

To eliminate artifacts, due to photo bleaching or linear absorption, we tested that the fluorescence signal increased as the square of the excitation intensity at the different excitation wavelengths for the different samples.

Photopolymer Preparation

For the evaluation of the 1,3-diketones as radical photoinitiators, an organic-inorganic silicate containing zirconium was employed.[87] It consisted of methacryloxypropyl trimethoxysilane (MAPTMS), methacrylic acid (MAA), and zirconium n-propoxide (ZPO, 70% in propanol).

MAPTMS was hydrolyzed using HCl solution (0.01 M) at a 1:0.75 ratio. ZPO was separately mixed with MAA, at 1:1 ratio. After 45 min, the hydrolyzed MAPTMS was added to the ZPO-MAA mixture. Finally, 31 mM of the investigated photoinitiator was added to each mixture. After stirring for 24 h, the materials were filtered using 0.22 µm syringe filters.

The samples were prepared by depositing a thick droplet onto a glass substrate, which were dried in a vacuum oven at 100 °C for 1 h before being processed by the laser.

3D structure fabrication by MPP. The experimental setup for the 3D structure fabrication by MPP has been described before.[88] For the multi-photon polymerization, a Ti:sapphire femtosecond laser was employed (Femtolasers Fusion, 800 nm, 400 mW average power, 75MHz repetition rate, with integrated dispersive mirrors that pre-compensate the beam delivery and focusing optics to achieve sub-20fs duration pulses into the sample). The 3D structure was 'written' using an x-y galvanometric mirror digital scanner (Scanlabs Hurryscan II), adapted to hold a high numerical aperture focusing microscope objective lens (100x, N.A. = 1.4, Zeiss, Plan Apochromat), and controlled using the SAMLight (SCAPS) software. The laser beam was expanded 5x using a telescope lens to improve focusing. Movement on the z-axis and large-scale movement on the x-y plane was achieved with a three-axes linear encoder stage (PI). The beam on/off was controlled using a mechanical shutter (Uniblitz), while its intensity was controlled by a motorized attenuator (Altechna). The stages, the shutter and the attenuator were computer-controlled via a National Instruments LabVIEW program. A CCD camera was mounted behind a dichroic mirror for the online monitoring of the polymerization.

The sample was mounted upside down with the glass slide facing the objective to prevent contact of the material with the oil of the objective, the structures were fabricated layer-by-layer, with the last layer on the surface of the coverslip; this was done to avoid illuminating through the already polymerized region. Scanning speed was always set at 2 mm/s, and the maximum laser power used was 70 mW, measured before the objective. After the completion of the component building process, the sample was developed in 4-methyl-2-pentanone for 20 min.

Conclusions

We have shown that the detailed design of push-pull dyes can lead to the formation of initiators in multiphoton photopolymerization with desirable properties. The attachment of a strong electron-withdrawing unit at position 9 of anthracene made it possible to maintain absorption maxima of α,β-unsaturated ketones in the green spectral region while broadening the absorption spectrum significantly. Elongation of the π-system did not cause a substantial red-shift of absorption. Indeed, replacing the 4-dimethylaminobenzylidene group with the electron-rich π-extended anthranylidene unit did not bathochromically shift the absorption of studied 1,3-diketones. The steric hindrance imparted by close proximity of two hydrogens at positions 1 and 8 of anthracene and the carbonyl groups forced the molecule to deviate from planarity. Conjugation was thus weakened in comparison to that observed for 2-(4-(dimethylamino)benzylidene-indene-1,3-dione.[35] The conjugation of proton sponge with cyclopentanone led to α,β-unsaturated ketone with slightly bathochromically shifted absoption and significantly red-shifted but very weak emission. Most importantly the maxima of two-photon absorption is 100 nm blue-shifted vs. values for analogous bis(4-dimethylaminobenzylidene)cyclopentanone. The combination of the above mentioned features and superb solubility allowed us to obtain photoinitiators with a fabrication window up to 40 mW, and a polymerization threshold starting as low as 8 mW, under the investigated experimental conditions. Since all studied ketones possessed very similar σ_2 at 800 nm, the differences in fabrication window are plausibly related to yield of triplet formation.

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References

1 Y.-H. Pao and P. M. Rentzepis, *Appl. Phys. Lett.,* 1965, **6**, 93-95.

2 S. Maruo, O. Nakamura and S. Kawata, *Opt. Lett.,* 1997, **22**, 132-134.

3 A. Marino, A. Desii, M. Pellegrino, M. Pellegrini, C. Filippeschi, B. Mazzolai, V. Mattoli and G. Ciofani, *ACS Nano,* 2014, **8**, 11869-11882.

4 O. Kufelt, A. El-Tamer, C. Sehring, S. S. Wolter and B. N. Chichkov, *Biomacromolecules,* 2014, **15**, 650-659.

5 C. M. Marco, A. Gaidukeviciute, R. Kiyan, S. M. Eaton, M. Levi, R. Osellame, B. N. Chichkov and S. A. Turri, *Langmuir,* 2013, **29**, 426-431.

6 H. -B. Sun and S. Kawata, *APS,* 2004, **170**, 169-273.

7 K. -S. Lee, D. -Y. Yang, S. H. Park and R. H. Kim, *Polym. Adv. Technol.,* 2006, **17**, 72-82.

8 K. D. Belfield, A. R. Morales, B. -S. Kang, J. M. Hales, D. J. Hagan, E. W. V. Stryland, V. M. Chapela and J. Percino, *Chem. Mater.,* 2004, **16**, 4634-4641.

9 J. M. Hales, D. J. Hagan, E. W. V. Stryland, K. J. Schafer, A. R. Morales, K. D. Belfield, P. Pacher, O. Kwon, E. Zojer and J. L. Bredas, *J. Chem. Phys.,* 2004, **121**, 3152-3160.

10 K. D. Belfield, K. J.Schafer, W. Mourad and B. A. Reinhardt, *J. Org. Chem.,* 2000, **65**, 4475-4481.

11 C. Martineau, R. Anémian, C. W. I. Andraud, M. Bouriau and P. L. Baldeck, *Chem. Phys. Lett.,* 2002, **362**, 291-295.

12 G. S. He, L.-S. Tan, Q. Zheng and P. N. Prasad, *Chem. Rev.,* 2008, **108**, 1245-1330.

13 M. Wang, X. Ma, J. Yu, X. Jia, D. Han, T. Zhou, J. Yang, J. Nie and T. Wang, *Polym. Chem.,* 2015, **6**, 4424-4435.

14 A. I. Ciuciu and P. J. Cywinski, *RSC Adv.,* 2014, **4**, 45504-45516.

15 B. H. Cumpston, S. P. Ananthavel, S. Barlow, D. L. Dyer, J. E. Ehrlich, L. L. Erskine, A. A. Heikal, S. M. Kuebler, I. Y. S. Lee, D. -M. Maughon, J. Qin, H. Rockel, M. Rumi, X. -L. Wu, S. R. Marder and J. W. Perry, *Nature,* 1999, **398**, 51-54.

16 J. Lalevee, P. Xiao, S. Telitel, M. Lepeltier, F. Dumur, F. M. Savary, D. Gigmes and J. P. Fouassier, *Beilstein J. Org. Chem.*, 2014, **10**, 863-876.

17 Z. Q. Li, J. Torgersen, A. Ajami, S. Muhleder, X. H. Qin, W. Husinsky, W. Holnthoner, A. Ovsianikov, J. Stampfl and R. Liska, *RSC Adv.*, 2013, **3**, 15939-15946.

18 R. Nazir, F. Bourquard, E. Balčiūnas, S. Smoleń, D. Gray, N. V. Tkachenko, M. Farsari and D. T. Gryko, *ChemPhysChem.*, 2015, **16**, 682-690.

19 R. Nazir, P. Danilevicius, A. I. Ciuciu, M. Chatzinikolaidou, D. Gray, L. Flamigni, M. Farsari and D. T. Gryko, *Chem. Mater.*, 2014, **26**, 3175-3184.

20 G. von Freymann, A. Ledermann, M. Thiel, I. Staude, S. Essig, K. Busch and M. Wegener, *Adv. Funct. Mater*., 2010, **20**, 1038-1052.

21 F. Hao, Z. Liu, M. Zhang, J. Liu, S. Zhang, J. Wu, H. Zhou and Y. Tian, *Spectrochimica Acta A: Mol. Biomol. Spectr*., 2014, **118**, 538-542.

22 Z. Li, N. Pucher, K. Cicha, J. Torgensen, S. C. Ligon, A. Ajami, T. Husinsky, A. Rosspeintner, E. Vauthey, S. Naumov, T. Scherzer, J. Stampfl and R. Liska, *Macromolecules*, 2013, **46**, 352-361.

23 N. Pucher, A. Rosspeintner, V. Satzinger, V. Schmidt, G. Gescheidt, J. Stampfl and R. Liska, *Macromolecules*, 2009, **42**, 6519-6528.

24 W. -E. Lu, X. -Z. Dong, W. -Q. Chen, Z. -S. Zhao and X.-M. Duan, *J. Mater. Chem*., 2011, **21**, 5650-5659.

25 R. Nazir, P. Danilevicius, D. Gray, M. Farsari and D. T. Gryko, *Macromolecules*, 2013, **46**, 7239-7244.

26 K. D. Belfield and K. J. Schafer, *ACS Symposium Series, Volume 847, Photoinitiated Polymerization*, Chapter 39, 2003, 464-481.

27 C. N. LaFratta, J. T. Fourkas, T. Baldacchini and R. A. Farrer, *Angew. Chem. Int. Ed.*, 2007, **46**, 6238-6258.

28 K. D. Belfield, K. J. Schafer, Y. Liu, J. Liu, X. Ren and E. W. Van Stryland, *J. Phys. Org. Chem*., 2000, **13**, 837-849.

29 (a) S. Maruo and J. T. Fourkas, *Laser Photonics Rev.*, 2008, **2**, 100-111; (b) W. Wu, R. Tang, Q. Li and Z. Li, *Chem. Soc. Rev.*, 2015, **44**, 3997-4022; (c) J.-F. Xing, M.-L. Zheng and X.-M. Duan, *Chem. Soc. Rev.*, 2015, **44**, 5031-5039.

30 S. Telitel, J. Lalevée, N. Blanchard, T. Kavalli, M. A. Tehfe,S. Schweizer, F. Morlet-Savary, B. Graff and J. P. Fouassier, *Macromolecules*, 2012, **45** , 6864-6868.

31 M. A. Tehfe, F. Dumur, B. Graff, F. Morlet-Savary, J. P. Fouassier, D. Gigmes and J. Lalevée, *Macromolecules*, 2012, **45**, 8639-8647.

32 S. Telitel, S. Schweizer, F. Morlet-Savary, B. Graff, T. Tschamber, N. Blanchard, J. P. Fouassier, M. Lelli, E. Lacôte and J. Lalevée, *Macromolecules*, 2013, **46**, 43-48.

33 M. A. Tehfe, F. Dumur, B. Graff, J. L. Clément, D. Gigmes, F. Morlet-Savary, J. P. Fouassier and J. Lalevée, *Macromolecules*, 2013, **46**, 736-746.

34 D. -L. Versace, F. Dalmas, J. P. Fouassier and J. Lalevée, *ACS Macro Lett.*, 2013, **2**, 341-345.

35 M. A. Tehfe, F. Dumur, B. Graff, D. Gigmes, J. P. Fouassier and J. Lalevée, *Macromolecules*, 2013, **46**, 3332-3341.

36 M. A. Tehfe, F. Dumur, B. Graff, D. Gigmes, F. Morlet-Savary, J. P. Fouassier, D. Gigmes and J. Lalevée, *Macromolecules* 2013, **46**, 3761-3770.

37 P. Xiao, F. Dumur, T. T. Bui, F. Goubard, B. Graff, F. Morlet-Savary, J. P. Fouassier, D. Gigmes and J. Lalevée, *ACS Macro. Lett.*, 2013, **2**, 736–740

38 P. Xiao, F. Dumur, D. Thirion, S. Fagour, A. Vacher, X. Sallenave, F. Morlet-Savary, B. Graff, J. P. Fouassier, D. Gigmes and J. Lalevée, *Macromolecules*, 2013, **46**, 6786–6793.

39 P. Xiao, F. Dumur, B. Graff, F. Morlet-Savary, L. Vidal, D. Gigmes, J. P. Fouassier and J. Lalevée, *Macromolecules,* 2014, **47**, 26-34.

40 K. Belfield, Proceedings of the Radtech Europe Confernce, vol. 2, Vincentz Network, Hannover, pp. 75-82.

41 S. Dadashi-Silab, C. Aydogan and Y. Yagci, *Polym. Chem.,* 2015, **6**, 6595-6615.

42 J. Torgersen, A. Ovsianikov, V. Mironov, N. Pucher, X. H. Qin, Z. Q. Li, K. Cicha, T. Machacek, R. Liska, V. Jantsch and J. Stampfl, *J. Biomed. Opt.*, 2012, **17**, 105008.

43 J. Torgersen, X. H. Qin, Z. Q. Li, A. Ovsianikov, R. Liska and J. Stampfl, *Adv. Funct. Mater.*, 2013, **23**, 4542-4554.

44 M. Chatzinikolaidou, S. Rekstyte, P. Danilevicius, C. Pontikoglou, H. Papadaki, M. Farsari and M. Vamvakaki, *Mater. Sci. Eng. C,* 2015, **48**, 301-309.

45 V. Melissinaki, A. A. Gill, I. Ortega, M. Vamvakaki, A. Ranella, J. W. Haycock, C. Fotakis, M. Farsari and F. Claeyssens, *Biofabrication*, 2011, **3**, 045005.

46 J. K. Gansel, M. Thiel, M. S. Rill, M. Decker, K. Bade, V. Saile, G. von Freymann, S. Linden and M. Wegener, *Science*, 2009, **325**, 1513–1515.

47 Y. -S. Chen, A. Tal and S. M. Kuebler, *Chem. Mater.*, 2007, **19**, 3858–3860

48 L. Amato, Y. Gu, N. Bellini, S. M. Eaton, G. Cerullo and R. Osellame, *Lab Chip*, 2012, **12**, 1135-1142.

49 M. H. Olsen, G. M. Hjorto, M. Hansen, O. Met, I. M. Svane and N. B. Larsen, *Lab Chip*, 2013, **13**, 4800-4809.

50 A. Radke, T. Gissibl, T. Klotzbucher, P. V. Braun and H. Giessen, *Adv. Mater.*, 2011, **23**, 3018–3021.

51 N. Vasilantonakis, K. Terzaki, I. Sakellari, V. Purlys, D. Gray, C. M. Soukoulis, M. Vamvakaki, M. Kafesaki and M. Farsari*, Adv. Mater.,* 2012, **24**, 1101–1105.

52 G. Kenanakis, A. Xomalis, A. Selimis, M. Vamvakaki, M. Farsari, M.; Kafesaki, C. M. Soukoulis and E. N. Economou, *ACS Photonics*, 2015, **2**, 287-294.

53 B. M. Monroe, W. K. Smothers, D. E. Keys, R. R. Krebs, D. J. Mickish, A. F. Harrington, S. R. Schicker, M. K. Armstrong, D. M. T. Chan and C. I. Weathers, *Imaging Sci*., 1991, **35**, 19-25.

54 J. Wu, Y. Zhao, X. Li, M. Shi, F. Wu and X. Fang, *New J. Chem.,* 2006, **30**, 1098-1103.

55 S. S. Sarkisov, B. H. Peterson, M. J. Curley, V. N. Nesterov, T. Timofeeva, M. Antipin, E. I. Radovanova, A. Leyderman and P. A. Fleitz, *J. Nonlinear Opt. Phys.*, 2005, **14**, 21-40.

56 Y. Zhao, W. Wang, F. Wu, Y. Zhou, N. Huang, Y. Gu, Q. Zou and W. Yang, *Org. Biomol. Chem.*, 2011, **9**, 4168-4175.

57 W. Yang, Q. Zou, Y. Zhou, Y. Zhao, N. Huang, Y. Gu and F. Wu, *J. Photochem. Photobiol. A,* 2011, **222**, 228-235.

58 D, Kim, H. Moon, S. H. Baik, S. Singha, Y. W. Jun, T. Wang, K. H. Kim, B. S. Park, J. Jung, I. Mook-Jung and K. H. Ahn, *J. Am. Chem. Soc.*, 2015, **137**, 6781-6789.

59 X. Cheng, K. Wang, S. Huang, H. Zhang and Y. Wang, *Angew. Chem. Int. Ed.*, 2015, **54**, 8369–8373.

60 J. Xue, Y. Zhao, J. Wu and F. J. Wu, *Photochem. Photobiol. A*, 2008, **195**, 261–266.

61 K. Yamashita, S. Imahashi and S. Ito, *Dyes Pigm.,* 2008, **76**, 748-753.

62 Q. Zou, Y. Zhao, N. S. Makarov, J. Campo, H. Yuan, D. C. Fang, J. W. Perry and F. Wu, *Phys. Chem. Chem. Phys*., 2012, **14**, 11743–11752.

63 R. Nazir, T. T. Meiling, P. J. Cywiński and D. T. Gryko, *Asian J. Org. Chem.*, 2015, **4**, 929-935.

64 B. Strehmel, A. M. Sarker and H. Detert, *ChemPhysChem.,* 2003, **4**, 249–259.

65 M. A. Tehfe, F. Dumur, B. Graff, D. Gigmes, F. Morlet-Savary, J. P. Fouassier, D. Gigmes and J. Lalev_em, *Macromolecules,* 2013, **46**, 3761–3770

66 T. Kusumoto, D. Kosumi, C. Uragami, H. A. Frank, R. R. Birge, R. J. Cogdell and H. Hashimoto, *J. Phys. Chem. A,* 2011, **115**, 2110-2119.

67 M. Planells and N. Robertson, *Eur. J. Org. Chem.*, 2012, **6**, 4947-4953.

68 F. Terenziani, C. Katan, E. Badaeva, S. Tretiak and M. Blanchard-Desce, *Adv. Mater*., 2008, **20**, 4641–4678.

69 F. Montigny, G .Argouarch and C. Lapinte, *Synthesis*, 2006, **2**, 293-298.

70 H. Cao, H. Zhan, J. Cen, J. Lin, Y. Lin, Q. Zhu , M. Fu and H. Jiang, *Org. Lett.*, 2013, **15**, 1080-1083.

71 P. Goswami and B. Das, *Tetrahedron Lett.*, 2009, **50**, 897-900.

72 R. Abonia, D. Insuasty, J. Castillo, B. Insuasty, J. Quiroga, M. Nogueras and J. Cobo, *Eur. J. Med. Chem.*, 2012, **57**, 29-40.

73 G. Audrey, D. Frederic, D. Eddy, M. Fabien, W. Guillaume and M. R. Cedric, *Org. Lett.*, 2010, **12**, 2382-2385.

74 N. V. Vistorobskii and A. F. Pozharskii, *Zh. Org. Khim.,* 1989, **25**, 2154-2161.

75 N. V. Vistorobskii, O. V.; Nogradopa and A. F. Pozharskii, *Russ. Chem. Bull.,* 1997, **46**, 334-336.

76 M. J. Frisch et al., Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT, 2013.

77 G. Lemercier, C. Martineau, J.-C. Mulatier, I. Wang, O. Stéphan, P. Baldeck and C. Andraud, *New J. Chem.*, 2006, **30**, 1606-1613.

78 F. Momicchioli, G. Ponterini and D. Vanossi, *Phys. Chem. Chem. Phys.,* 2014, **16**, 15576-15589.

79 K. M. Shafeekh, S. Das, C. Sissa and A. Painelli, *J. Phys. Chem. B,* 2013, **117**, 8536-8546.

80 W. J. Yang, C. H. Kim, M. -Y. Jeong, S. K. Lee, M. J. Piao, S. -J. Jeon and B. R. Cho, *Chem. Mater.*, 2004, **16**, 2783-2789.

81 B. Strehmel, S. Amthor, J. Schelter and C. Lambert, *ChemPhysChem.*, 2005, **6**, 893-896.

82 D. S. Pedersen and C. Rosenbohm, *Synthesis* 2001, **16**, 2431–2434.

83 R. R. Tykwinski, M. Schreiber, R. P. Carlón, F. Diederich and V. Gramlich, *Helv. Chim. Acta,* 1996, **79**, 2249-2281.

84 M. Samoc, A. Samoc, G. T. Dalton, M. P. Cifuentes, M. G. Humphrey, P. A. Fleitz, I. Rau and F. Kajzar, eds, Old City Publishing, Philadelphia, (2011), Chapter 7, pp. 341-355.

85 C. A. Schneider, W. S. Rasband and K. W. Eliceiri, *Nature Methods,* 2012, **9**, 671-675.

86 N. S. Makarov, M. Drobizhev and A. Rebane, *Optics Express,* 2008, **16**, 4029-4047.

87 A. Ovsianikov, J. Viertl, B. Chichkov, M. Oubaha, B. MacCraith, I. Sakellari, A. Giakoumaki, D. Gray, M. Vamvakaki, M. Farsari and C. Fotakis, *ACS Nano*, 2008, **2**, 2257–2262.

88 I. Sakellari, E. Kabouraki, D. Gray, V. Purlys, C. Fotakis, A. Pikulin, N. Bityurin, M. Vamvakaki and M. Farsari, *ACS Nano,* 2012, **6**, 2302–2311.

Table of contents graphic:

Non-planar, two-photon absorbing α,β-unsaturated 1,3-diketones possessing anthracene moiety are efficient photoinitiators in direct laser writing.