New chlorin-e_6 trimethyl ester compounds as holographic data storage media at liquid helium temperature

Dieter Franzke,[a] Hansruedi Gygax,[b] Alois Renn,[c] Urs P. Wild,[c] Heinz Wolleb[d] and Heinz Spahni[d]

[a] *General Energy Research, Paul Scherrer Institute, CH-5232 Villigen, Switzerland*
[b] *Givaudan-Roure Research LTD, CH-8600 Dübendorf, Switzerland*
[c] *Physical Chemistry Laboratory, Swiss Federal Institute of Technology, ETH Zentrum, CH-8092, Zürich, Switzerland*
[d] *Corporate Research Units, Ciba-Geigy Limited, Marly Research Center, CH-1723 Marly, Switzerland*

The chlorin–polyvinylbutyral (PVB) guest–host system has been the workhorse for most of the previously reported holographic hole burning experiments. In order to extend the spectral range and to improve on some of its properties we synthesized chlorin-e_6 trimethyl ester **1** and brominated chlorin-e_6 trimethyl ester **2**, which require a much shorter synthesis pathway than chlorin. We studied the hole burning behaviour of these new dyes with different matrix materials and film preparation methods at liquid helium temperature and measured important properties like hole width and burning kinetics. One result was that we found the methyl ester compounds embedded into a photopolymer to have a five times faster burning rate than the chlorin–photopolymer system.

In recent years, persistent spectral hole burning (SHB) has revealed an unshared potential for high density information storage.[1–6] In combination with holography up to 12 000 holograms have been stored in a single chlorin-polyvinylbutyral (PVB) film.[7] Though the memory properties of this dye-in-polymer system are already impressive and many efforts have been made to optimize the storage device, the perfect system has not yet been found. The dye should have a broad inhomogeneous absorption band but a small homogeneous line width because the maximum number of different holograms which can be stored in one sample is limited by the ratio of the homogeneous line width and the inhomogeneous broadening. To obtain permanent spectral holes the dye has to undergo a photoreaction to a product with an absorption band in a different spectral region which is, at least at liquid helium temperature, stable against thermal back-reaction. A Debye–Waller factor close to 1 is required as well as a high quantum efficiency of the burning process and a good contrast of the spectral hole. It is also desirable that the dye is commercially available or easy to synthesize.

Though being the passive part of the system, the choice of the matrix is also of great importance. The dye solubility should be sufficiently high to yield films with an optical density of 1–2, even for samples with a thickness of only a few microns. The films have to display good optical quality, *i.e.* flat surface and no tarnish. Further it is known that the matrix can affect the homogeneous line width and the temporal stability of the holes.[8,9]

Our most promising results were previously obtained with chlorin in a PVB matrix. The 'figure of merit' of this system is shown in Fig. 1. It was the goal of a recent research project to find new systems which extend the spectral range of the chlorin–PVB system without losing its exceptional qualities and which require a less sophisticated synthesis. In this paper, we report the synthesis and hole burning properties of two chlorin analogues which can be derivatized from commercially available materials.

Experimental

Synthesis of chlorin-e_6 trimethyl ester 1 and brominated chlorin-e_6 trimethyl ester 2

In contrast to the complex synthesis of chlorin[10] we used the method described below to get to **1** and **2**. Apart from ease of synthesis the two compounds have the advantage that the introduction of the methyl ester groups improves the solubility of the dye in polymer matrices. The bromine atom was brought in because we expected the photochemical reaction to be accelerated by the 'heavy-atom effect'.[11] The photochemistry of our molecules is assumed to occur during relaxation *via* the triplet state. Therefore an increase of the intersystem crossing (ISC) rate, which can be induced by 'heavy atoms', enhances the probability of photoproduct formation.

Chlorin-e_6 trimethyl ester 1. To 400 ml of degassed MeOH in a 1 l round-bottomed flask, equipped with magnetic stirrer, reflux condenser and thermometer, were added 2 g (3.36 mmol) of chlorin e_6. The resulting black suspension was degassed with argon for 10 min and then 20 ml of conc. H_2SO_4 in 200 ml of degassed MeOH were added within 15 min. The resulting green solution was refluxed for 1 h. The reaction mixture was cooled to room temp., poured on 1 l of iced water and neutralized to pH 7 with solid $NaHCO_3$. The aqueous phase was extracted with ethyl acetate (2 × 700 ml). The combined organic phases were washed twice with 100 ml of brine, dried with $MgSO_4$, filtered and evaporated. Flash chromatography (ethyl acetate then MeOH) afforded 1.80 g (84%) of **1** as a violet powder. TLC (propanol–ethyl acetate–H_2O–25% aq.

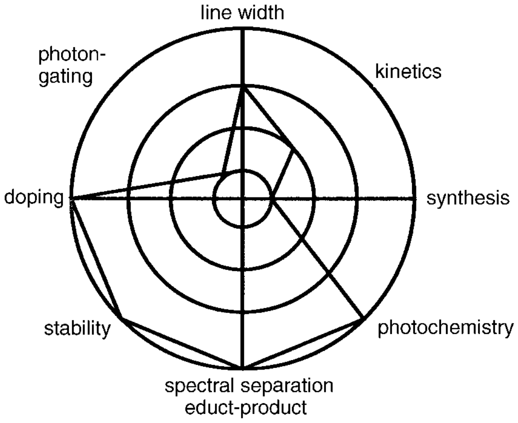
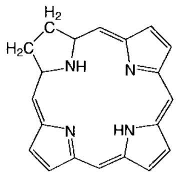
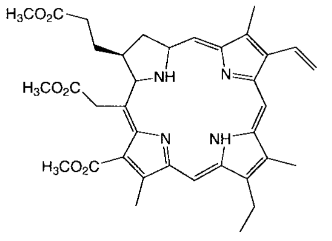


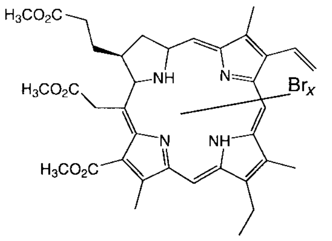
Fig. 1 Figure of merit of chlorin: points on the outer circles indicate good properties, and points on the inner circles poor properties



chlorin
$C_{20}H_{16}N_4$



chlorin-e_6 trimethyl ester **1**
$C_{37}H_{40}N_4O_6$



brominated chlorin-e_6 trimethyl ester **2**
$C_{37}H_{40-x}N_4O_6Br_x$

Fig. 2 Chemical structures of chlorin, chlorin-e_6 trimethyl ester **1** and brominated chlorin-e_6 trimethyl ester **2**

NH_3, 70:10:20:10): $R_f=0.67$; UV (*N*-methylpyrrolidine): λ_{max}/nm 662. δ_H [300 MHz, $(CD_3)_2SO$] 9.79 (s, 1H, β-H); 9.68 (s, 1H, α-H); 9.11 (s, 1H, δ-H); 8.35 (dd, 1H, *J* 12, *J* 18, 2a-H_X); 6.44 (dd, 1H, *J* 1, *J* 18, 2b-H_B); 6.15 (dd, 1H, *J* 1, *J* 12, 2b-H_A); 5.95 (d, 1H, *J* 18, 10-CH); 5.41 (d, 1H, *J* 18, 10-CH); 4.60 (m, 1H, 8-H); 4.31 (m, 1H, 7-H); 3.81 (m, 2H, 4a-CH_2); 3.62; 3.58; 3.55; 3.51; 3.35; 3.33 (6s, 18H, 9a-CH_3, 10b-CH_3, 7d-CH_3, 5a-CH_3, 1a-CH_3, 3a-CH_3); 2.7–1.4 (m, 4H, 7a,7b-CH_2); 1.69 (t, 3H, *J* 7, 8a-CH_3); 1.61 (d, 3H, *J* 7, 4b-CH_3).

Brominated chlorin-e_6 trimethyl ester 2. In a 50 ml round-bottomed flask, equipped with magnetic stirrer and thermometer were placed 0.836 g (1.31 mmol) of chlorin-e_6 trimethyl ester **1** in 200 ml of $CHCl_3$. A solution of 0.21 g (1.31 mmol) of bromine in 5 ml of $CHCl_3$ was added within 5 min at -10 °C under an argon atmosphere. The reaction mixture was warmed to room temp. within 20 min and then evaporated. Flash chromatography (ethyl acetate then MeOH) afforded 0.649 g (72%) of **2** as a violet powder. δ_H [300 MHz, $(CD_3)_2SO$] showed that the product was a mixture of isomers, with bromination at the C2a—C2b double bond and the *meso* positions, mainly at the β-position. TLC (propanol–ethyl acetate–H_2O–25% aq. NH_3, 70:10:20:10): $R_f=0.57$. UV (NMP): λ_{max}/nm 656 (Found: C, 60.39; H, 6.15; N, 7.24; Br, 7.80. Calc. for $C_{37}H_{39}BrN_4O_6$: C, 62.09; H, 5.49; N, 7.83; Br, 11.16%).

Sample preparation

For our holographic data storage experiments we need homogeneous films of high optical quality, *i.e.* flat surfaces, a perfect transparency and a high optical density (OD 1–2) at the absorption maximum of the dye. If experiments are performed to make use of the Stark effect, very thin samples are required (< 50 μm) to achieve a homogeneous and strong electric field on the sample. We used three methods to prepare our samples.

Casting. On a glass plate with a freshly cleaned, flat surface a glass cylinder of *ca.* 3–5 cm diameter is mounted by gluing. This cylinder is filled with a solution of polymer, dye and an appropriate solvent. The amount of polymer is calculated in such a way that after evaporation of the solvent the desired film thickness is reached. The concentration of the dye is determined by the desired optical density. The glass cylinder is then covered partially by a glass plate and the solvent is allowed to evaporate in a place with no air turbulence. By this method, films of thicknesses 40–200 μm can be produced.

If a polymer with a low glass transition or melting point is used, the quality can be improved by a subsequent step: the film on the glass plate is covered with a second glass plate and pressed while it is heated to a temperature a few degrees below its melting point. After a few hours the homogeneity of the film has improved, bubbles are removed and the thickness has decreased. This method is limited to thermoplastic polymers which have a melting point which is sufficiently below the decomposition point of the embedded dye.

Spin coating. The dye–polymer solution is placed on to the centre of a freshly cleaned glass substrate which is mounted on a fast rotating stage. By centrifugal force a film of homogeneous thickness is formed. The properties of the resulting films are determined by various process parameters, such as rotation speed, acceleration, time, sample volume, concentration and viscosity. This coating method, which can be automated easily, is especially suited for films with a thickness below 10 μm. If the viscosity of the solution used is too high the surface of the resulting films is mostly very rough.

Photopolymerization. For this approach, we dissolved the dyes in an epoxy oligomer solution of Ebecryl 600 (straight epoxyacrylate based oligomer from UCB) and Darocur 1173 (photoinitiator for UV curing from Ciba-Geigy), which was kindly supplied as a stock solution by Dr M. Köhler of the Additive Division Ciba-Geigy. A few ml of the stock solution were introduced carefully between two glass plates which were kept apart by thin spacers. After 2 s of irradiation with a xenon arc lamp we obtained homogeneous polymer films of approximately 200 μm thickness. The optical quality was very good. This method is restricted to dyes which are soluble in the photopolymer and also to dyes which do not undergo an irreversible photoreaction upon UV irradiation. In the case of chlorin and its derivatives this method worked well.

Investigation of photochemical and photophysical properties

For a first examination of our samples we utilized the optical setup shown in Fig. 3. A dye laser (Lambda Physik FLD 3002) is pumped by an excimer laser (Lambda Physik LPX 130). The beam is expanded to 0.5 cm diameter and is then directed to the sample which was placed into a flow cryostat (Oxford Instruments) in a UV photospectrometer (Perkin-Elmer Lambda 9). After irradiation, the sample is rotated by 90° for measurements. Although the spectral resolution of this instrument (0.2 nm) is much broader than the expected spectral hole width, we used this setup because it allowed us a relatively fast test of some material properties. This method allowed us, for example, to see whether a certain sample shows hole burning at all and to detect the spectral position of the photoproduct as well.

For a quantitative comparison between chlorin and its two derivatives **1** and **2** with respect to the kinetics, line width and hole stability, we used a setup[12] as in Fig. 4. The beam of a Coherent autoscan dye laser is divided into two parts which

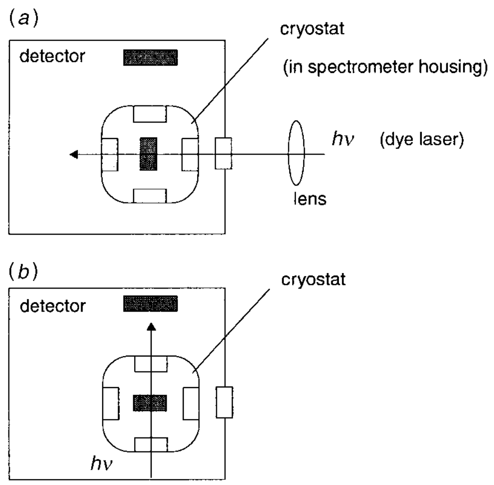


Fig. 3 Setup for testing the hole burning properties; the sample was brought into a cryostat which was built in a UV spectrometer. After irradiation (*a*) the sample holder could be turned from outside by 90° for measurements of the absorption spectra (*b*).

are combined on the sample again to write a holographic grating. The setup allows us to measure the transmitted light of one of the beams as a function of time. If one of the writing beams is blocked and the other one attenuated, the hologram written can be detected and by spectral scanning with the read-out laser beam, the line width of the hologram (diffraction mode) can be obtained as well as the line width in transmission mode.

For measurements of the fluorescence lifetime at room temp. we used the setup described in ref. 13. The method of time-correlated single-photon-counting (TCSPC) was used. The light source consists of a Coherent Antares mode-locked Nd:YAG laser and a home built synchronously pumped dye laser. This system supplies at 76 MHz repetition rate pulses of *ca.* 10 ps duration. The emission is detected with a Spex 1400 double monochromator equipped with a photomultiplier tube.

Results and Discussion

We started with poly(methyl methacrylate) (PMMA) as matrix, since it is a standard polymer with good optical properties, and built samples of **1** and **2** by the spin coating technique described above. On glass substrates with *ca.* 2 mm thickness we prepared PMMA–dye films with a thickness of 5–10 µm with optical densities between 1 and 3. We tried several solvents and found that the best results were obtained with isobutyl methyl ketone. In this case the optical quality of the films was obviously very good. The naked eye could detect no inhomogeneities. The samples were brought to the setup described in the Experimental section (Fig. 3) and cooled to *ca.* 5 K. Comparing the absorption spectra of the samples at room temperature and at 5 K we found that on cooling the absorption band gets narrower, the peak is shifted a few nm to the blue and the optical density at this point increases. This effect is already known.[14] The following experiments were performed with Rhodamine 101 as laser dye. In the case of **2**–PMMA we first tried to burn a hole at 657.5 nm which was at the maximum of the absorption. The area of irradiation was *ca.* 1 cm^2 and the pulse energy was estimated to be 0.5 mJ pulse^{-1} at the sample. After 100 000 pulses only a small hole could be observed and the OD dropped from *ca.* 1.2 to 1.125. With a burning wavelength of 650 nm we did not manage to burn a detectable hole though the energy per pulse at this wavelength was twice as much as in the case before. Slightly better results were obtained with **1**–PMMA. Subsequently, spectral holes could be burnt at 662.5, 656.5 and 659.5 nm. But when we burnt at 659.5 nm we observed that the hole at 662.5 nm was partially refilled while the hole at 659.5 nm remained unchanged. In summary, the **1**–PMMA and **2**–PMMA systems are not very appropriate devices for data storage.

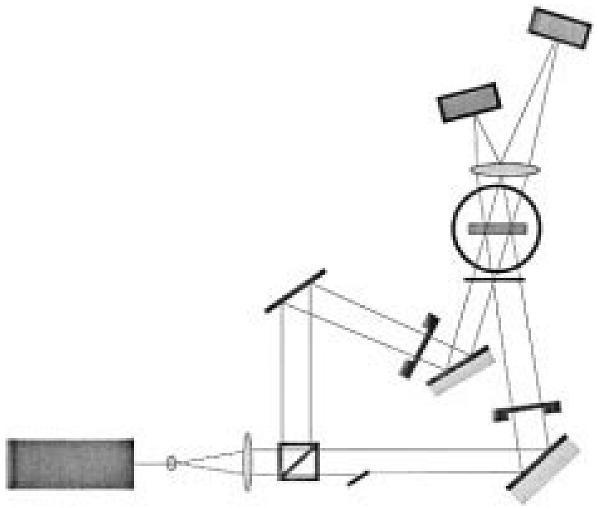


Fig. 4 Setup for quantitative measurements of hole burning properties. It allowed measurement in absorption and in holographic mode, respectively. The setup has been described in detail in a previous publication (ref. 12).

Next we embedded **1** and **2** in the photopolymer as described in the 'Photopolymerisation' section above. After cooling to 5 K we burnt several holes at 646.5–660.5 nm. The pulse energies at the sample were 0.2–1 mJ cm^{-2}. Also, we observed a refilling of existing holes if new ones were burnt at shorter wavelengths. A typical experiment is shown in Fig. 5. In trace (*a*) the result of an experiment is shown where a spectral hole was burnt at 652 nm in a sample of **1** embedded in photopolymer. The laser was operated at 20 Hz for 500 s (10 000 pulses). Trace (*b*) was recorded after providing 5000 pulses at 648 nm to the same sample. Another 5000 pulses at 648 nm [trace (*c*)] results in a significantly deeper hole at this position while the hole at 652 nm meanwhile clearly shows refilling. Traces (*d*)–(*f*) show subsequent hole burning experiments at 646 and 656 nm, respectively, which also cause a decrease in the holes previously burnt. After having burnt these holes we recorded the UV spectra over a larger range, as shown in Fig. 6 and we could observe the formation of a new absorption maximum centred at *ca.* 600 nm which is due to the photoproduct. For technical reasons this experiment could not be performed at the same resolution as the measurements shown in Fig. 5 and therefore the single holes in the main absorption

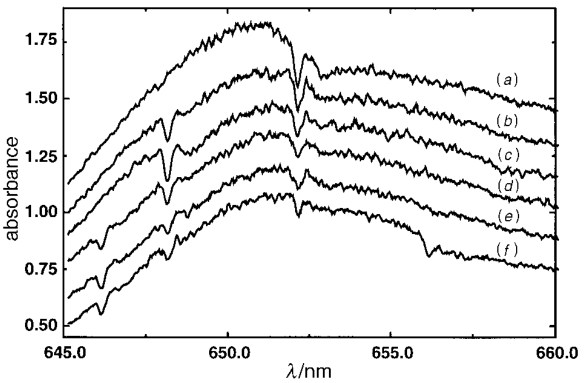


Fig. 5 Holes formed in the absorption band of **1** in the photopolymer also showing hole refilling. For details see text.

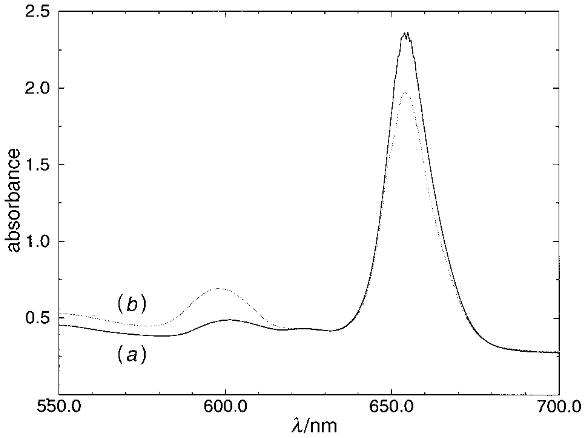


Fig. 6 Larger range UV–VIS spectrum of **1** (*a*) before and (*b*) after irradiation, also showing photoproduct formation indicated by a new absorption band at *ca.* 600 nm. In this spectrum several holes which were burnt around the absorption maximum are not resolved.

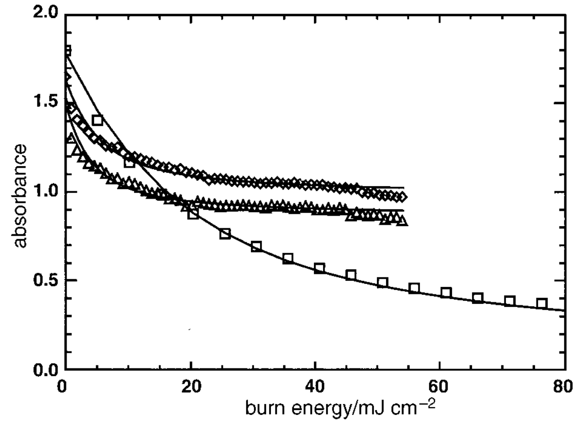


Fig. 7 Burning kinetics. The modified chlorins burn at similar burning efficiencies five times faster; (□) chlorin (26 mJ cm^{-2}), (△) **1** (5.5 mJ cm^{-2}) and (◇) **2** (7.2 mJ cm^{-2}).

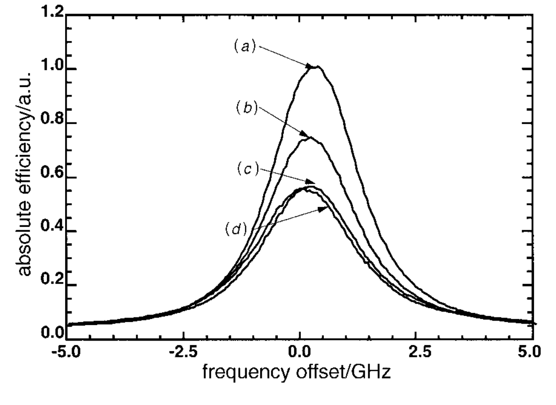


Fig. 8 Temporal hologram stability of chlorin in photopolymer: (*a*) 0 min, 2.05 GHz; (*b*) 5 min, 2.19 GHz; (*c*) 30 min, 2.46 GHz; (*d*) 45 min, 2.52 GHz

band after irradiation are not resolved. Only an overall decrease of the absorption is observed. When the temperature then was raised to 293 K the absorption band of the photoproduct had disappeared again and the original spectrum of **1** was obtained with no changes from its appearance prior to cooling and burning. With **2** in the photopolymer we obtained similar results. The range where holes could be burnt was 646–666 nm, somewhat broader than in the case of **1**. As seen with compound **1** we observed a photoproduct with an absorption maximum at 600 nm. In this case we tried to burn spectral holes in the photoproduct. At 595, 600 and 605 nm stable holes could successfully be detected.

After these experiments which showed that hole burning was in principle possible with our new samples we made a comparison with the well known chlorin and embedded this substance in a photopolymer also.

Now we used the setup described in the Experimental section (Fig. 4) to measure the kinetics of the hole burning processes, the hole widths and the time stability of the holes. With the setup shown in Fig. 4, a holographic grating was written. During the writing procedure the transmission of the sample was recorded. After the burning process the hole was detected in two ways. First we made a scan around the burning frequency using a laser power much lower than that used during the burning process. In addition the hole width was determined holographically which is a more accurate method because it is background free. The measured values were fitted with an exponential decay curve and as shown in Fig. 7 the burning rate of **1** and **2** is about five times faster than for chlorin itself. The hole widths of the new compounds, however, are up to 50% larger. This is a drawback in terms of the maximum theoretical storage density which can be achieved. Furthermore, we investigated the hole stability of chlorin in the photopolymer for comparison with the well known chlorin–PVB system. For this purpose we burnt a hole at 636.09 nm, then held the sample at liquid helium temperature without further bleaching and measured the hole depth as well as line width as a function of time (Fig. 8). These measurements showed that the photopolymer is worse than PVB. Another quantity we determined was the Debye–Waller factor of chlorin in the photopolymer. The higher this number the more of the absorption band can be used for SHB. It was found to be 0.55, which is in the same range as for chlorin–PVB (0.65).

As one of the quantities of interest in a photochemical reaction is the fluorescence lifetime we did some room temperature measurements with the setup described in ref. 13. For the same matrix, *i.e.* photopolymer, Table 1 shows that the lifetimes of **1** and chlorin have almost the same value, while the lifetime of the brominated species **2** is significantly shorter. In addition, we observe a strong matrix effect; the lifetimes of the new compounds embedded in PMMA are much shorter than in the photopolymer (Table 1).

Conclusions

From the results described in this paper, we can conclude that **1** and **2** are good alternatives to chlorin for use as data storage materials at liquid helium temperature. Their synthesis is much easier than that of chlorin and they show five-fold faster burning kinetics. The spectra of both compounds are shifted *ca.* 20 nm to the red compared to chlorin. Almost over the whole inhomogeneous bandwidth, spectral holes can be burnt which are stable for reasonable times. The absorption spectra of these compounds as well as the spectra of their photoproducts show no overlap with the spectra of chlorin in the region useful for SHB. Therefore it is possible to build up films consisting of a matrix, chlorin and one of these new compounds. This leads to an extension of the spectral range which can be used for data storage. The hole burning properties of **1** and **2** are almost identical though we assumed the brominated compound to be faster by enhancing the ISC rate due to the presence of the 'heavy atom'. The fluorescence lifetime measurements at room temperature show that the decay of the excited state of **2** is faster than that of **1** and decay of both is faster than that of chlorin.

The photopolymer which we used showed very good optical properties and the preparation of the samples could be performed very quickly. Disadvantages, however, are the broader

Table 1 Comparison of selected properties of chlorin and compounds **1** and **2** in different matrices[a]

material	abs. max./nm	abs. max. photoprod./nm	burning rate	hole stability	fluorescence lifetime/ns
chlorin–PVB	634	580	+	++	8
chlorin–photopol.			+	+	7.5
1–PMMA	662		−	−	0.96
1–photopol.	652	598	++	+	6.14
2–PMMA	657		−	−	0.61
2–photopol.	654	598	++	+	3.02

[a] ++: very good, + good, − poor.

line width and the faster decay times of holes burnt into chlorin–photopolymer compared to chlorin–PVB. This behaviour might be improved if the photopolymer mixture is modified such that the network built during photopolymerization is less flexible.

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