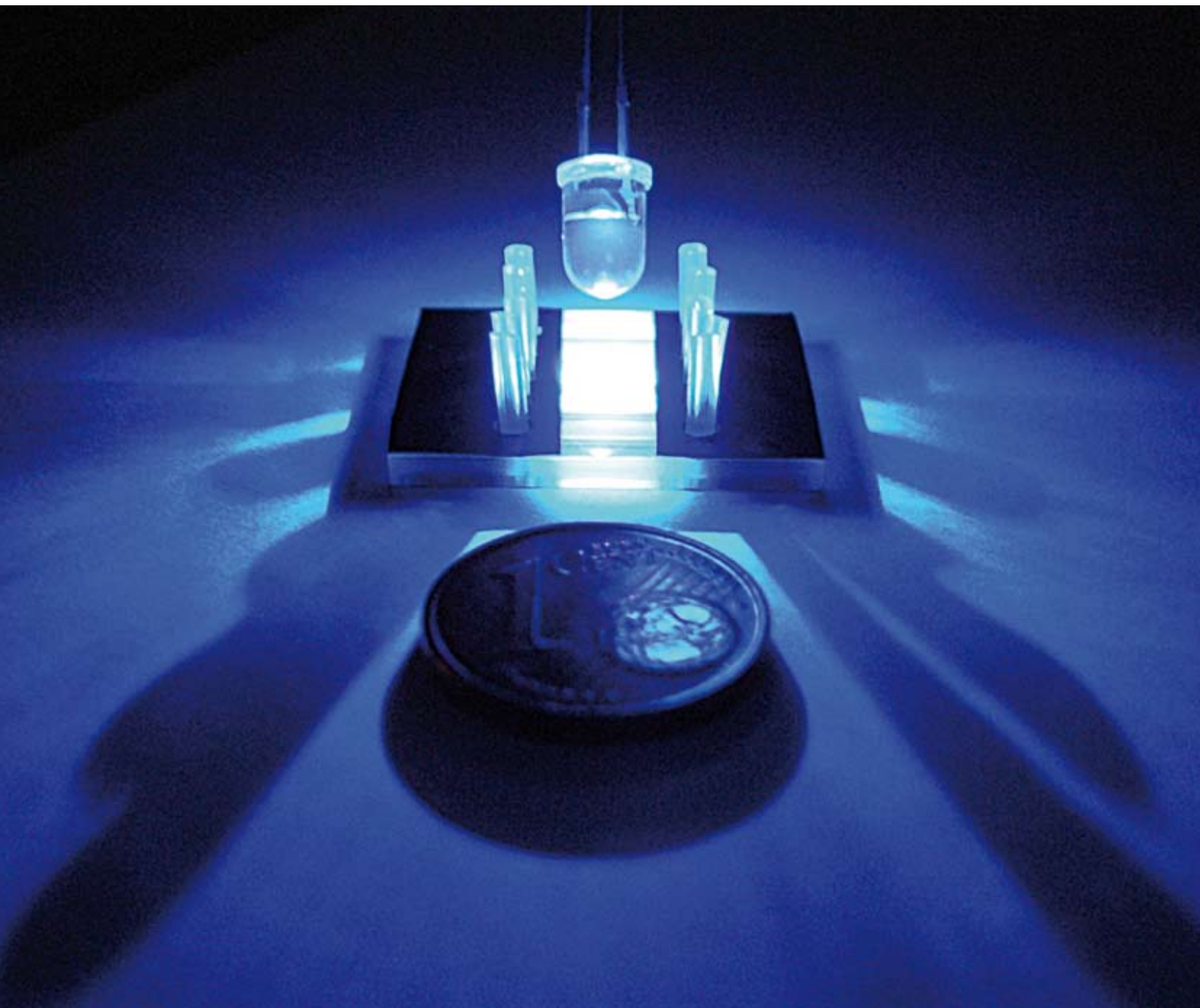


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UV-LED photopolymerised monoliths†

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For the first time photopolymerisation of polymer monoliths has been realised with UV-light emitting diodes (LEDs) as light source and demonstrated with polymethacrylate monoliths created in fused silica capillaries and plastic chips.

Since the first synthesis of macroporous polymeric monoliths by photoinitiated polymerisation in 1997 by Svec and co-workers¹ there have been different approaches to photopolymerisation and a variety of applications shown over the last decade.^{1,2} The advantage of photopolymerisation in comparison to the conventional methods (thermal or red-ox initiation of polymerisation) is primarily in the ability to create a monolithic microcolumn in a desired section of capillary or chip.²⁻⁷ So far for photopolymerisations only classical UV light sources have been used, namely incandescent and discharge lamps, mercury and xenon arc lamps, UV tubes or fluorescent blacklight lamps.^{2,4,8} These UV sources have been incorporated in a variety of UV curing equipment, such as photochemical reactors,⁹ UV-crosslinker^{1,10-12} or other light sources generating UV radiation. Most of them provide the desired wavelength by applying various filters to a polychromatic light source, yielding to a narrow spectrum with a specific wavelength maximum, typically at 360 nm or 254 nm.

Light emitting diodes (LEDs) introduced in the 1960's in the electronics industry¹³ have later found use as light sources for optical analytical techniques.¹⁴ As a typical example, over the last decade LEDs were used in miniaturised photometric detectors for capillary electrophoresis resulting in lower baseline noise and correspondingly improved detection limits.¹⁴⁻¹⁸ LEDs offer numerous advantages, including robustness of the solid-state technology, typically low cost, long life time, small heat generation and small size compatible with modern trends in miniaturised instrumentation.¹³ Only relatively recently UV-LEDs have become commercially available and quickly found a wide range of applications, including fluorescent detection of fraudulent documents, in forensic investigations, antique identification, in disinfecting devices, etc.

In this work UV-LEDs are demonstrated for the first time as light sources for photopolymerisation of monoliths. Using a

255 nm or 370 nm UV-LED, polymethacrylate monoliths were prepared by photoinitiated polymerisation in transparent fused silica capillaries and within the channels of microfluidic chips. While it was shown that the new UV-LED photopolymerised monoliths had comparable properties with those prepared by classical technology, the well defined spectra of the LEDs facilitated an investigation of wavelength matching between the UV-LED and the photoinitiator.

A range of UV-LEDs is available^{13,19} with specified emission maxima ranging from 395 nm in intervals of 5 nm down to 245 nm thus providing a quasi continuous coverage of most of the UV region. The choice of LEDs as well as photoinitiators (PI)²⁰ used for photopolymerisations was based on matching their emission and absorption wavelength maxima; for this work two pairs of LED-photoinitiator were selected and are captured in Table 1.

2,2'-Dimethoxy-2-phenylacetophenone (DAP) has been widely used as a photoinitiator in photopolymerisations.^{2,3,12} 4,4'-Bis(dimethylamino)benzophenone or Michler's ketone (MK) has been extensively used for photopolymerisation of photosensitive compositions together with benzophenone.^{21,22} Although generally the aim of this study was to demonstrate the use of UV-LEDs for photopolymerisations under the most typical conditions used, in the case of MK it was deliberately chosen as the sole initiator without benzophenone to keep the absorption spectra of the polymerisation mixture simple. To the best of the author's knowledge Michler's ketone has not been used in photopolymerisations as the only initiator.

Methacrylic monoliths were synthesised using glycidyl methacrylate (GMA) as a main monomer and ethylene dimethacrylate (EDMA) as a crosslinker. A mixture of cyclohexanol and decanol was used as porogenic solvent.²

The photopolymerisation experiments followed generally well established procedures^{2,3,23} with details in the ESI.† The general setup is shown in Fig. 1A and B. The LED (255 nm or 370 nm, see Table 1) was positioned at a distance of 0 to 30 mm (*L* in Fig. 1) from the capillary or chip and capillary/chip was exposed to UV light for the desired length of time (5–60 min).

Table 1 LEDs and photoinitiators (PI) used

LED ^a emission max./nm	PI ^b absorption max./nm	PI chemical name and acronym
255	255	2,2'-Dimethoxy-2-phenylacetophenone (DAP)
370	370	4,4'-Bis(dimethylamino)benzophenone [Michler's ketone (MK)]

^a LEDs used: 255 nm from Sensor Electronic Technology, Ltd; 370 nm from Roithner Lasertechnik, GmbH. ^b Ref. 20.

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† Electronic supplementary information (ESI) available: Pretreatment of fused silica capillaries or channels of microfluidic chips; photopolymerisation; SEM characterisation; backpressure characterisation; microfabrication of microfluidic chip; EOP measurements. See DOI: 10.1039/b802693a

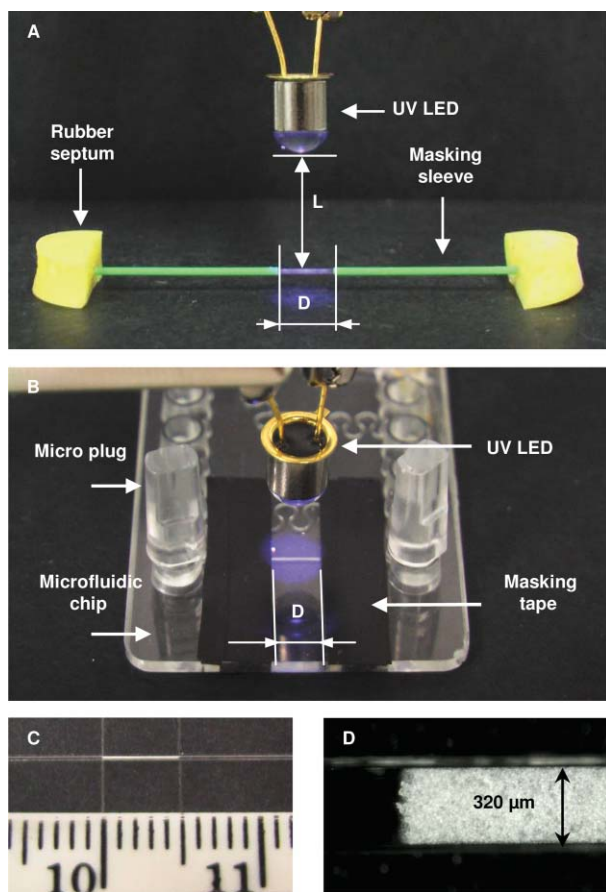


Fig. 1 Experimental setup for UV-LED photopolymerisation. A. Polymicro transparent poly(tetrafluoroethylene) coated fused silica capillary, 100 μm id, microtight sleeve used for masking, $L = 20\text{--}30$ mm, $D = 3\text{--}5$ mm. B. Top view of a microfluidic chip (channel N5, width/depth 320 μm , cyclo-olefin copolymer (COC) snake mixer slide SMS0104 from ThinXXS Microtechnology AG), $L = 5$ mm, $D = 4$ mm. C. Optical image of formed monolith in a fused silica capillary with the white lines underneath marking where the mask was positioned. D. Optical image of formed monolith in the channel of microfluidic chip. Conditions for C and D: Photopolymerisation: 30% (C) or 40% (D) methacrylic monomers GMA/EDMA = 50/50 (v/v), porogenic solvent cyclohexano/decanol = 1/2, initiator MK (1% to monomer), 370 nm LED, $L = 20$ mm (C) or $L = 30$ mm (D), LED current 20 mA, exposure time 60 min (C) or 10 min (D).

For optimal LED-PI combination the distance L of LED from the capillary (chip) was important in terms of monolith's quality and especially the sharpness of the monolith edges and their exact matching of the masked position. The optimal LED distance from capillary was found to be at 20–30 mm from the capillary for the 370 nm LED, and 5–10 mm for the 255 nm LED. This reflects primarily the need to achieve the necessary UV-radiation energy density, which decreases with increasing distance and is generally lower for lower wavelengths (the 255 nm and 370 nm LEDs have specified outputs of 0.5 and 1.4 mW cm^{-2} at 20 mA, respectively).

The irradiation time and LED power with respect to monolith formation were found to be optimal at 5–10 min for LED currents between 20 and 80 mA.

As a general rule good quality monoliths with sharp edges as illustrated in Fig. 1C and D were obtained both for fused

silica capillaries and microfluidic chips when the LED and PI pairs were of matching emission-absorption spectra maximum wavelengths: DAP—255 nm LED and MK—370 nm LED (Table 1). These results are logical²⁴ and therefore to be expected in terms of optimal energy uptake by the initiator when its spectra is matched with LED emission maximum. It has to be noted that in the works reported in the literature it is not uncommon that excitation at 365 nm is used in combination with an initiator absorbing at approx. 255 nm.¹²

The morphology of the formed monoliths as well as the attachment to the capillary walls was assessed and the pore size estimated using scanning electron microscopy (SEM). SEM images of representative examples for both the DAP and MK initiated monoliths presented in Fig. 2 do not show any apparent differences to monoliths obtained using classical UV light sources. Use of 30 to 40% of monomer in the polymerisation mixture resulted in a porous monolith with pore size of approx. 2 μm , which is again comparable to typical literature data.⁴ The SEM images also confirmed a good attachment of polymer to the walls of capillaries.

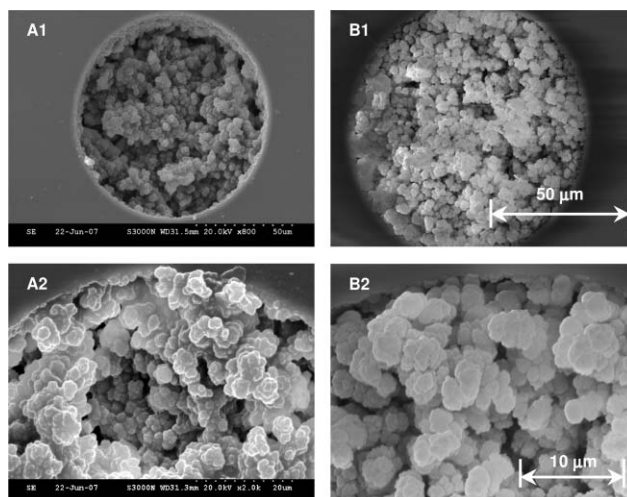


Fig. 2 SEM images of photopolymerised methacrylate (GMA/EDMA) monoliths, LED current 20 mA, exposure time 10 min. Conditions: A. 255 nm LED, $L = 5$ mm, initiator DAP, 30% of monomer, A1—magnification 800 \times , A2—another cut, magnification 2.0k. B. 370 nm LED, $L = 30$ mm, initiator MK, 40% of monomer, B1—magnification 1.0k, B2—magnification 4.0k.

The backpressure characteristics of the obtained monoliths showed that the higher the LED power and/or the polymerisation time used the denser (with smaller pores) was the obtained monolith (Table 2).

Importantly, the measured values of 6–56 bar cm^{-1} are in the range of monolith backpressure values normalised for the same conditions (100 μm id, 1 $\mu\text{l min}^{-1}$, water, 20 $^{\circ}\text{C}$) as used previously⁴ for the same concentration of methacrylic monomers and the same exposure time (10 min). This shows that photopolymerisations with a single UV-LED can deliver the same functional parameter monolith as for the conventional 500 W HgXe UV lamp used by Rohr *et al.*⁴

Finally an attractive application for the UV-LED photopolymerised monoliths is presented as an on-chip electro-osmotic micro-pump (EOP) following previous work by Nie

Table 2 Backpressure values of methacrylate monoliths^a

Time/min	LED power/mA	Backpressure/bar cm ⁻¹ , 1 $\mu\text{l min}^{-1}$, H ₂ O, 20 °C
10	20	6 ^b
5	80	6 ^b
10	80	45
20	80	56

^a Photopolymerisation conditions: 40% methacrylic monomers GMA/EDMA = 50/50 (v/v), 370 nm LED, $L = 0$ mm, initiator DAP.

^b Literature value of 0.5 MPa (ref. 4) over the monolith of 8.5 cm at a flow rate 0.1 $\mu\text{l min}^{-1}$ corresponds to 5.9 bar cm⁻¹ at a flow rate 1 $\mu\text{l min}^{-1}$ under the conditions as in Table 2.

et al.^{25,26} where chip-embedded commercial silica monoliths were used. A polymethylmethacrylic (PMMA) chip with micromilled channels (10 mm \times 0.4 mm \times 0.4 mm) was used for photopolymerisations of GMA/EDMA to create a monolithic electro-osmotic pump (EOP). 15% and 30% polymer containing monolithic channels were compared to open channel (no monolith inside) using a 0.2 mM sodium acetate buffer (pH 3.5) as an electrolyte. Open channel and both monolithic EOPs showed a linear relationship between the applied voltage and the current measured (Fig. 3).

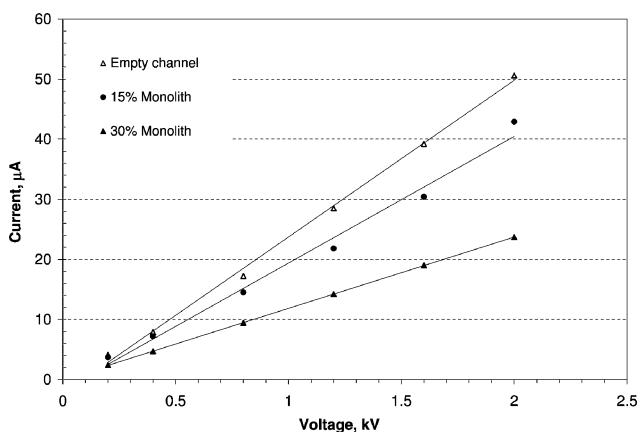


Fig. 3 Relationship between the applied voltage and the current measured for methacrylic monoliths* photopolymerised in the channels (0.4 \times 0.4 mm) of the PMMA chip showing monolithic EOP function. Electrolyte: 0.2 mM CH₃COONa (pH 3.5). * Photopolymerisation conditions: 30% or 15% of methacrylic monomers GMA/EDMA = 50/50 (v/v), porogenic solvent cyclohexano/decanol = 1/2, initiator DAP (1% to monomer), 255 nm LED, $L = 2$ mm, LED current 20 mA, exposure time 30 min.

In general, the more monomer used for monolith synthesis the smaller the EOP and current values measured, as with higher concentrations of monomer denser monolith was created resulting in a lower effective channel cross-section.²⁶ This shows that such monoliths can be used as on-chip electro-osmotic micro-pumps which is one of the main applications for the UV-LED polymerised monoliths in this laboratory.

The results presented here show for the first time UV-LED photopolymerisation as a simple, elegant way to create short

sections of monolithic columns in capillaries and channels of microfluidic chips. As the optical power of UV-LEDs grow and their prices fall in the future, they are likely to become an attractive alternative to the classical UV-light sources used so far. Research in this laboratory is currently underway in utilising UV-LED photopolymerised monoliths as electro-osmotic micro-pumps and chromatographic microcolumns.^{25,26}

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Notes and references

- 1 C. Viklund, E. Ponten, B. Glad, K. Irgum, P. Horstedt and F. Svec, *Chem. Mater.*, 1997, **9**, 463–471.
- 2 D. Lee, F. Svec and J. M. J. Fréchet, *J. Chromatogr., A*, 2004, **1051**, 53–60.
- 3 T. Rohr, C. Yu, M. H. Davey, F. Svec and J. M. J. Fréchet, *Electrophoresis*, 2001, **22**, 3959–3967.
- 4 T. Rohr, E. F. Hilder, J. J. Donovan, F. Svec and J. M. J. Fréchet, *Macromolecules*, 2003, **36**, 1677–1684.
- 5 C. Yu, F. Svec and J. M. J. Fréchet, *Electrophoresis*, 2000, **21**, 120–127.
- 6 C. Yu, M. Xu, F. Svec and J. M. J. Fréchet, *J. Polym. Sci., Part A: Polym. Chem.*, 2002, **40**, 755–769.
- 7 F. Svec, T. B. Tennikova and Z. Deyl, *Monolithic Materials: Preparation, Properties and Applications*, Elsevier, The Netherlands, 2003.
- 8 J. Wen, C. Guillo, J. P. Ferrance and J. P. Landers, *Anal. Chem.*, 2006, **78**, 1673–1681.
- 9 M. Kato, K. Sakai-Kato, T. Toyo'oka, M. T. Dulay, J. P. Quirino, B. D. Bennett and R. N. Zare, *J. Chromatogr., A*, 2002, **961**, 45–51.
- 10 M. T. Dulay, J. P. Quirino, B. D. Bennett, M. Kato and R. N. Zare, *Anal. Chem.*, 2001, **73**, 3921–3926.
- 11 M. Kato, M. T. Dulay, B. D. Bennett, J. P. Quirino and R. N. Zare, *J. Chromatogr., A*, 2001, **924**, 187–195.
- 12 I. M. Lazar, L. Li, Y. Yang and B. L. Karger, *Electrophoresis*, 2003, **24**, 3655–3662.
- 13 S. Landgraf, in *Handbook of Luminescence, Display Materials, and Devices*, 2003, vol. 3, pp. 372–398.
- 14 P. K. Dasgupta, I. Y. Eom, K. J. Morris and J. Z. Li, *Anal. Chim. Acta*, 2003, **500**, 337–364.
- 15 M. Macka, P. Andersson and P. R. Haddad, *Electrophoresis*, 1996, **17**(12), 1898–1905.
- 16 M. King, B. Paull, P. R. Haddad and M. Macka, *Analyst*, 2002, **127**(12), 1564–1567.
- 17 C. Johns, M. Macka and P. R. Haddad, *Electrophoresis*, 2003, **24**(12–13), 2150–2167.
- 18 J. P. Hutchinson, C. J. Evenhuis, C. Johns, A. A. Kazarian, M. C. Breadmore, M. Macka, E. F. Hilder, R. M. Guijt, G. W. Dicinoski and P. R. Haddad, *Anal. Chem.*, 2007, **79**(18), 7005–7013.
- 19 http://www.roithner-laser.com/LED_UV_SEOUL.htm, 12.02.2008.
- 20 http://www.sigmaaldrich.com/aldrich/brochure/al_pp_applications.pdf, 12.02.2008.
- 21 *US Pat.*, WO 8001846 A1, 1980.
- 22 *JP Pat.*, 48019682 B, 1973.
- 23 F. Svec, *Electrophoresis*, 2006, **27**, 947–961.
- 24 J. D. Coyle, R. R. Hill and D. R. Roberts, *Light, chemical change and life: a source book in photochemistry*, The Open University Press, UK, 1982.
- 25 F.-Q. Nie, M. Macka and B. Paull, *Lab Chip*, 2007, **7**, 1597–1599.
- 26 F.-Q. Nie, M. Macka, L. Barron, D. Connolly, N. Kent and B. Paull, *Analyst*, 2007, **132**, 417–424.