

Thin-film organic photodiodes as integrated detectors for microscale chemiluminescence assays

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Abstract

We report the use of thin-film organic photodiodes as integrated optical detectors for microscale chemiluminescence. The copper phthalocyanine–fullerene (CuPc–C₆₀) small molecule photodiodes have an external quantum efficiency of ~30% at 600–700 nm, an active area of 2 mm × 8 mm and a total thickness of ~2 nm. Simple detector fabrication, based on layer-by-layer vacuum deposition, allows facile integration with planar chip-based systems. To demonstrate the efficacy of the approach, CuPc–C₆₀ photodiodes were used to monitor a peroxyoxalate based chemiluminescence reaction (PO-CL) within a poly(dimethylsiloxane) (PDMS) microfluidic device. Optimum results were obtained for applied reagent flow rates of 25 μL/min, yielding a CL signal of 8.8 nA within 11 min. Reproducibility was excellent with typical relative standard deviations (R.S.D.) below 1.5%. Preliminary quantitation of hydrogen peroxide yielded a detection limit of ~1 mM and linearity over at least three decades. With improved sensitivity and when combined with enzymatic assays the described integrated devices could find many applications in *point-of-care* diagnostics.

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1. Introduction

Chemiluminescence (CL) is a common detection method for liquid phase analysis [1]. CL reactions typically involve the formation of a metastable reaction intermediate or product in an electronically excited state. Subsequent light emission can result directly from the excited compound returning to the ground state (direct CL) or via an energy transfer process to a suitable fluorophore (indirect CL) [2]. While luminol or lucigenin based direct CL has found widespread analytical applications, indirect peroxyoxalate CL (PO-CL) based methods are surprisingly limited. This is in part due

to the low solubility and CL efficiency of oxalate esters in aqueous media. However, the addition of surfactants or microemulsions can overcome these limitations [3]. In organic solvents, PO-CL based methods yield high CL quantum efficiencies [4] and can be used in conjunction with a wide range of fluorophores [5]. To minimize interference from quenching or enhancing compounds and increase selectivity, CL is often used for post-separation detection [6–8] or coupled with specific enzymatic reactions [9]. Since the CL reaction acts as an internal light source, instrumental requirements are low. The minimal background signal also results in very low detection limits. All these characteristics make CL amenable for high sensitivity multi-analyte detection in microfluidic systems [10,11]. The small dimensions typically encountered in microfluidic devices enhance diffusion based reagent mixing while the reaction rate and CL

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output can be conveniently controlled via the applied flow rate [12].

In previous reports of CL detection within microfluidic environments the CL signal was detected and quantified using externally mounted photomultiplier tubes (PMTs) [8,12]. However, recently, Jorgensen et al. have reported the use of integrated silicon photodiodes for monitoring CL reactions within microfluidic systems [13]. Although, the authors demonstrate an elegant and efficient fluidic system for integrated CL detection, fabrication of the silicon photodiodes involved a series of complex doping, deposition and patterning steps. An alternative approach is to use solution-processable semiconducting polymers or vacuum deposited small molecule organic semiconductors, which offer simpler routes to device fabrication and tunable optical properties. These characteristics have been extensively demonstrated for thin-film polymer light emitting diodes (pLEDs) which are now entering the market place for simple display applications [14–16]. Interestingly such devices, which comprise one or more layer of organic semiconducting material sandwiched between two electrodes, not only emit light under electrical excitation but can also generate a measurable current under illumination [17]. The photovoltaic effect in organic photodiodes is based on the formation of electron–hole pairs (excitons) and subsequent dissociation and charge collection at the electrodes. While photo-induced charge generation is enhanced by large interfaces between electron donor and acceptor materials, good connectivity to the collection electrodes must also be ensured. Photodiodes based on interpenetrating networks formed from phase-segregated polymers [18] have demonstrated quantum efficiencies >80% under zero bias [19]. Comparable efficiencies, bandwidths and faster response times of $\sim 1 \mu\text{s}$ can be obtained by using small molecule organic materials [20]. With alternating multilayers of copper phthalocyanine (CuPc) and 3,4,9,10-perylenetetracarboxylic bisbenzimidazole (PTCBI), quantum efficiencies up to 80% have been reported under reverse bias [21]. As an alternative acceptor material with longer exciton diffusion length, the fullerene C_{60} has been successfully used in bilayer [22] and blend heterojunction devices [23] for solar cell applications, yielding high power conversion efficiencies.

The work presented herein is aimed at extending the application of organic photodiodes from solar cells to optical detectors in microfluidic systems. We report the successful integration of CuPc– C_{60} small molecule photodiodes with polydimethylsiloxane (PDMS) microfluidic devices for the monitoring of PO-CL reactions. For quantitation hydrogen peroxide was selected as a model compound because it is produced by a number of enzymes when in contact with specific analytes and dissolved oxygen (e.g. alcohol, glucose, cholesterol) [24]. Integrated portable detection systems for hydrogen peroxide could thus find widespread applications in *point-of-care* diagnostics.

2. Experimental

2.1. Microfluidic set-up

CL microfluidic devices were fabricated in-house from poly(dimethylsiloxane) (PDMS). Using a Sylgard 184 Silicone Elastomer kit (Dow Corning, Coventry, UK), monomer and hardener were mixed at a ratio of 10:1 (w/w), degassed for 30 min and then poured into a flat molding dish. After curing at 95°C for 1 h the $840 \mu\text{m}$ thick PDMS layer was peeled off and attached to a chromium coated glass plate (Nanofilm, Westlake Village, CA, USA). Structuring of the PDMS was performed by cutting the channels with a scalpel blade. The layout of the CL microdevices is shown schematically in Fig. 1. The device comprises two inlets, a straight mixing channel and an outlet. For quantitation experiments a microfluidic layer with a third inlet was also used. All inlets are $1000 \mu\text{m}$ wide, $840 \mu\text{m}$ deep and 1 cm long. The main channel is $1000 \mu\text{m}$ wide, $840 \mu\text{m}$ deep and 8 cm long. Channels were sealed by placing a 3 mm thick PDMS slab in conformal contact with the structured PDMS layer. Fluidic access holes at the channel ends were punched with a blunt $394 \mu\text{m}$ ID, $711 \mu\text{m}$ OD syringe needle (BD, Oxford, UK). Capillaries were inserted through the access holes to serve as fluidic reservoirs ($150 \mu\text{m}$ ID, $367 \mu\text{m}$ OD, Composite Metal Services, Hallow, UK). For flow generation a PHD 2000 syringe pump (Harvard Apparatus, Edenbridge, UK) with two 1 mL Bee Stinger gastight syringes (BAS, West Lafayette, IN, USA) was employed. The syringes were connected to 1.6 mm ID high-pressure fingertights (VWR, Poole, UK) via $762 \mu\text{m}$ ID PEEK tubing (Supelco, Bellefonte, PA, USA). The outlet of the fingertights comprised $356 \mu\text{m}$ ID Teflon tubing (Anachem, Luton, UK) which could be connected to the capillary reservoirs of the CL microdevices.

2.2. Organic photodiode fabrication

The fabrication of the CuPc– C_{60} heterojunction organic photodiodes and the effect of composition and architecture on device performance is described in detail elsewhere [23]. In short, the devices were fabricated on 1 mm thick indium-tin-oxide (ITO) coated glass substrates (CRL Opto, Hayes, UK) after initial cleaning by ultrasonication with acetone and methanol for 20 min each. The organic layers were grown by vacuum deposition in a Spectros system with a base pressure of about 8×10^{-8} mbar (Kurt J. Lesker Company, Hastings, UK). The organic materials used in the devices were 97% grade CuPc (Sigma-Aldrich, Gillingham, UK), twice purified by thermal gradient sublimation prior to deposition, and 99.5% C_{60} (MER Corp., Tucson, AZ, USA), used as received. For the photodiodes employed in the flow optimization experiments 58 nm thick layers comprising 60% (w/w) CuPc and 40% (w/w) C_{60} were deposited. The mixed layers were grown by co-deposition from independent organic evaporation sources, with the deposition rates monitored by a series

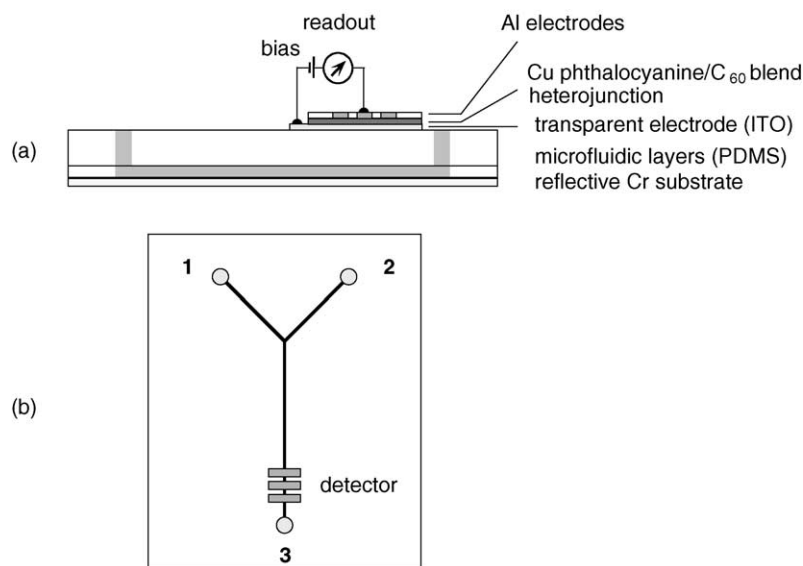


Fig. 1. (a) Side view of CuPc–C₆₀ photodiode integrated with planar PDMS microchip. A chromium coated glass plate serves as a reflective backside substrate. (b) Layout of PDMS microchip comprising two inlets (1, 2), mixing channel and outlet (3). Mixing channel is 1000 μm wide, 840 μm deep and 8 cm long. Positioning of the photodiode was above the mixing channel 52 mm downstream of the point-of-confluence of the two reagents. Only one of the three detection strips was used for the current studies (active area 2 mm \times 8 mm).

of quartz-crystal microbalances. For the bi-layer devices employed for hydrogen peroxide quantitation, CuPc and C₆₀ layers were deposited on top of each other at a thickness of 20 and 40 nm, respectively. This was followed by deposition of a 12 nm thick layer of twice sublimed 98% bathocuproine (BCP) (Sigma-Aldrich). One hundred nanometer thick Al electrodes were then deposited in situ by evaporation through a shadow mask yielding three detection strips with an active area of 2 mm \times 8 mm each. Finally the devices were encapsulated in a nitrogen atmosphere using an epoxy resin and glass coverslip. In the current studies, only the photocurrent of one detection strip was recorded, with the active area being considerably larger than the 1000 μm wide channels in the microfluidic structure. External quantum efficiencies (electrons out/ photons in) were determined using a 20 W ASB-W-020 tungsten–halogen lamp, a computer controlled CM110 monochromator (both CVI Technical Optics, Onchan, UK) and a Keithley 6517A electrometer for measuring induced photocurrents (Keithley Instruments, Reading, UK). System calibration was performed against a silicon photodiode.

2.3. Chemiluminescence materials

For flow optimization experiments, PO-CL reagents were extracted from Cyalume[®] hi-intensity white lightsticks (American Cyanamid Company, Charlotte, VC, USA). The active components are bis (2-carboxypentyloxy-3,5,6-trichlorophenyl) oxalate (CPPO), 9,10-diphenylanthracene dye (both reagent A) and hydrogen peroxide (reagent B) [25]. For quantitation experiments, hydrogen peroxide solutions were diluted in acetonitrile from a 31% (w/w) aqueous stock solution (all Sigma-Aldrich). To increase CL-

intensity, 5 mM 4-dimethylaminopyridine (DMAP) was used as a catalyst (Lancaster Synthesis, Morecambe, UK). All solutions were prepared daily and stored at 4 °C. Prior to introduction into the microfluidic device all solutions were degassed by ultrasonication for 1 min and filtered using 0.45 μm pore size PVDF syringe filters (Whatman, Clifton, NJ, USA).

2.4. Microscale chemiluminescence

To facilitate filling of the microchip, ethanol was first introduced through the inlets at 50 $\mu\text{L}/\text{min}$ and then replaced with CL reagents. For flow optimization experiments reagents A and B were pumped through inlets 1 and 2, respectively. The organic photodiode with the ITO side facing downwards was placed on top of the PDMS microchip and positioned 52 mm downstream of the point-of-confluence of the reagents, with the detector strip arranged perpendicular to the microchannel. For hydrogen peroxide quantitation experiments with a modified microfluidic layer, reagent A, DMAP and analyte were introduced through inlets 1, 2 and 3, respectively. To maximise sensitivity the bi-layer detector strip was positioned along the microchannel. Recording of the CL signal started with application of reagent flow to the inlets. Between experiments microfluidic channels were typically flushed with ethanol at 50 $\mu\text{L}/\text{min}$ for 5 min. All experiments were performed in the dark. The photocurrent was measured without applied bias using a Keithley 6514 electrometer. Data were smoothed using a built-in moving average filter function (average of 10 readings, 10 ms each). Data acquisition via the RS232 port and a computer controlled LabView[®] interface was performed at a sampling rate of 1 Hz.

3. Results and discussion

Prior to application of the integrated detectors to on-chip monitoring of PO-CL reactions the optical properties of the CuPc–C₆₀ blend heterojunction photodiodes [23] were characterised. Typical dark currents without applied bias were ~1 nA. The measured external quantum efficiency over the visible range is depicted in Fig. 2. While the quantum efficiency is above 5% over the whole visible range, maximum values of ~30% were recorded between 600 and 700 nm. Importantly, this closely corresponds to emission spectra of commonly used fluorophores such as Rhodamine B (λ_{\max} 625 nm) and Cy5 (λ_{\max} 666 nm), allowing application in many bioanalytical assays. While the quantum efficiency of these devices is inferior to efficiencies afforded by conventional silicon based photodiodes, CuPc based photodiodes with optimised device architecture can yield efficiencies up to 80% [21]. Furthermore the comparatively simple fabrication, small size and array compatibility render organic photodiodes particularly amenable as integrated detectors in microfluidic systems.

The choice of substrate material for the microfluidic chip was governed by a rapid prototyping capability and compatibility with the organic solvents required for the PO-CL reaction. While PDMS microchips are typically fabricated by molding methods [26], masters for deep microchannels with high optical path length can be difficult to fabricate. Consequently we explored a simple approach for fabricating deep PDMS microchannels by first casting a 840 μm thick PDMS slab, followed by cutting of a 1000 μm wide channel structure with a scalpel blade. Total fabrication times were of the order of 2 h per microchip (including device design, PDMS curing and channel structuring). Compatibility of PDMS with the organic solvents required for PO-CL was confirmed by a recent study showing that dimethylformamide (DMF) and acetonitrile only cause negligible swelling [27]. However, potential chemical oxidation of PDMS by hydrogen peroxide has to be

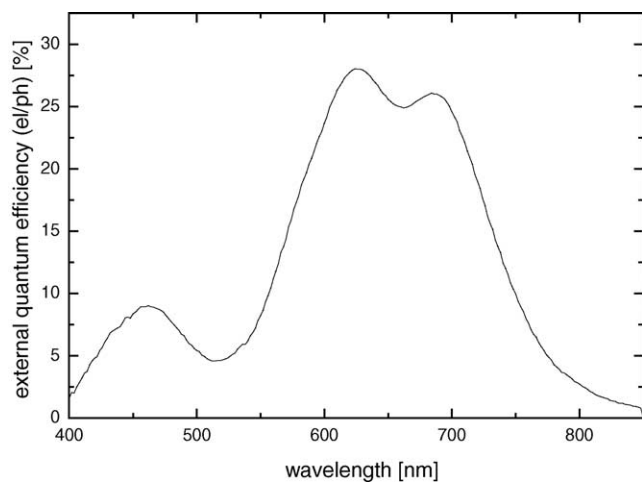


Fig. 2. External quantum efficiency over visible range for CuPc–C₆₀ photodiodes.

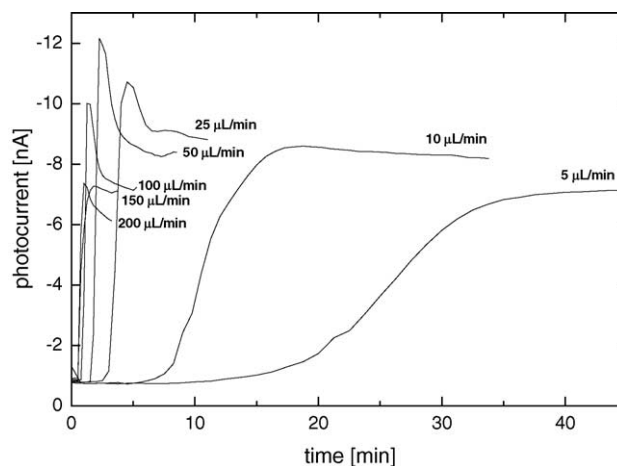


Fig. 3. Optimization of PO-CL reaction on PDMS microchip by monitoring with CuPc–C₆₀ photodiode. CPPO/diphenylanthracene and hydrogen peroxide were applied to inlets 1 and 2, respectively. The applied flow rate of both reagents was varied to optimise the mixing time and maximise the CL signal intensity. For easier viewing the data was spline fitted.

considered also. Oxidation was indeed observed during initial PO-CL experiments, resulting in slightly translucent PDMS microchannels with improved wettability. This greatly facilitated filling of the PDMS microchannels.

For PO-CL experiments, reagents 1 and 2 were hydrodynamically pumped through microchip inlets 1 and 2, respectively. Applied flow rates were optimised for yielding a large and reproducible CL signal within the shortest possible time. For all applied flow rates between 5 and 200 $\mu\text{L}/\text{min}$ two co-flowing streams were observed. This is consistent with calculated Re numbers between 0.2 and 8, indicative of a laminar flow regime where mixing occurs by diffusion only ($Re < 2000$). The time dependence of the CL signal varied significantly with applied flow rate, as shown in Fig. 3. Since the signal is produced by the CL reaction of reagents 1 and 2, the crucial parameter to optimise is the microchannel mixing. For applied flow rates of 5 and 10 $\mu\text{L}/\text{min}$, average linear velocities of 0.2 and 0.4 mm/s and residence times of 260 and 130 s are calculated, respectively. For the oxidising reagent, hydrogen peroxide, this equates to effective diffusion distances of 800 and 400 μm , respectively (based on a diffusion coefficient $1.2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$). Considering the channel width of 1000 μm and two co-flowing streams this allows for near complete intermixing of the reagents prior to reaching the detector. At low flow rates a gradual increase of CL signal followed by plateau formation is thus observed.

However, for flow rates of 25 $\mu\text{L}/\text{min}$ and higher the CL signal increases initially, but then decreases before plateauing out. We attribute this overshoot to the velocity profile induced by pressure driven flow. For an applied flow rate of 25 $\mu\text{L}/\text{min}$, average residence times for hydrogen peroxide molecules in the channel centre and at 10% channel width can be calculated as 26 and 73 s, respectively. This results in limited CL reaction and lower signal intensities in the channel centre and near the point-of-confluence. When the parabolic

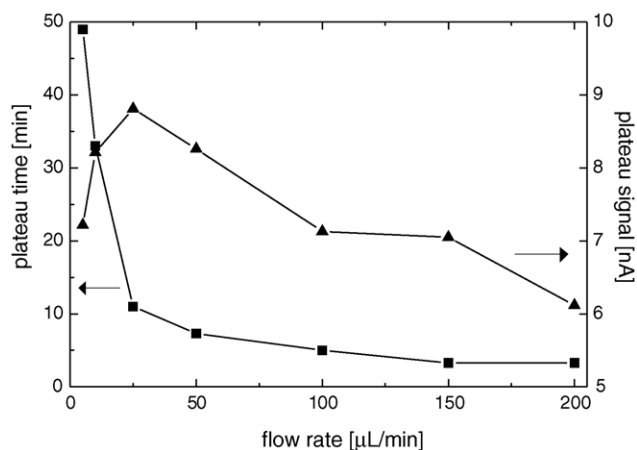


Fig. 4. Effect of applied flow rate on time required for plateau formation and on plateau CL signal intensity. Conditions as for Fig. 3.

flow front passes the detector a steep signal increase followed by a decrease and plateau formation can be observed. For higher flow rates the resulting plateau signal decreases due to progressively incomplete mixing. An overview of the effect of flow rate on the time required for plateau formation and CL signal intensity is shown in Fig. 4. It can be seen that optimum results are obtained at a flow rate of $25 \mu\text{L}/\text{min}$, yielding a CL signal of 8.8 nA within 11 min. While shorter analysis times are afforded by higher flow rates the CL signal is also reduced, resulting in lower sensitivity when applied to quantitative analysis.

For the optimised $25 \mu\text{L}/\text{min}$ flow conditions, reproducibility of the CL signal was determined by repeating experiments three times on the same microchip using identical reagent solutions. The corresponding CL signal versus time plots are depicted in Fig. 5. It can be seen that the plots

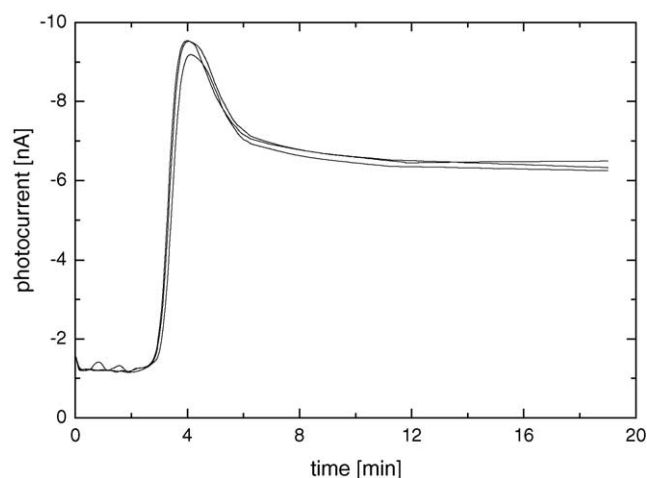


Fig. 5. Reproducibility of CuPc-C₆₀ photodiode response for monitoring of PO-CL reaction on PDMS microchip. The applied flow rate was $25 \mu\text{L}/\text{min}$ for both reagents. Experiments were performed on the same day with identical solutions. Between runs the microchip was flushed with ethanol at $50 \mu\text{L}/\text{min}$ for 20 min. Note that a different batch of CuPc-C₆₀ photodiodes was used compared to Fig. 3.

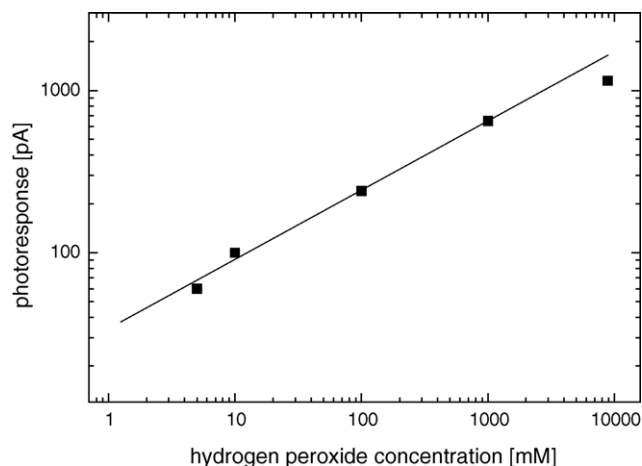


Fig. 6. Quantitation results for model compound hydrogen peroxide. The applied flow rate was $25 \mu\text{L}/\text{min}$ for all reagents. Baseline photocurrent ($\sim 0.3 \text{ nA}$) was subtracted from the measured plateau values. Note that bilayer CuPc-C₆₀ photodiodes were employed.

are highly reproducible with appreciable variations occurring only in the overshooting phase. For the steady-state signal after $\sim 11 \text{ min}$, R.S.D. values are below 1.5% ($n = 3$). This reproducibility is clearly sufficient for quantitative analysis and demonstrates the potential of both microchip based PO-CL and integrated detection with CuPc-C₆₀ photodiodes.

As a model compound hydrogen peroxide was quantified using this approach. The CL photoresponse as a function of hydrogen peroxide concentration is plotted in Fig. 6. A linear relationship between photoresponse and hydrogen peroxide concentration is obtained between $\sim 1 \text{ mM}$ and 1 M . For higher concentrations a deviation from linearity is observed, presumably due to the limited excess of CPPO reagent. Currently the detection limit is estimated slightly below 1 mM which is adequate for the monitoring of fermentation processes. While this preliminary detection limit is inferior to $\sim 5 \mu\text{M}$ reported for CL detection in microchannels using an integrated silicon photodiode [13], a significant sensitivity enhancement is expected through optimization of the organic photodiode composition and architecture.

4. Conclusions and outlook

Novel CuPc-C₆₀ photodiodes were characterised and applied as integrated detectors for the monitoring of PO-CL reactions within microfluidic devices. The employed organic photodiodes exhibit good responsivity in the visible range with quantum efficiencies up to 30% between 600 and 700 nm. Even higher efficiencies can be achieved with state of the art organic devices. Within a PDMS microchip, mixing of the PO-CL reagents was optimised via changes in the applied flow rates. Optimum results were obtained for $25 \mu\text{L}/\text{min}$ yielding CL signals of 8.8 nA within 11 min. Reproducibility of the measured photocurrent was excellent with typical R.S.D. values below 1.5% ($n = 3$). Quantitation of the model

compound hydrogen peroxide yielded a preliminary detection limit of ~ 1 mM and a linear response over at least three decades, which is adequate for the monitoring of fermentation processes.

While the presented results clearly demonstrate the effectiveness of microscale PO-CL and of integrated CuPc–C₆₀ photodiode detection, research into PO-CL compatible fluorescent labels is ongoing to widen the field of potential applications. Combining multiple fluorescent labels with integrated organic photodiode arrays offers a direct route towards real-time, multi-analyte detection within microfluidic analysis systems. It should be noted that the performance of such systems will ultimately be limited by the sensitivity of the photodiodes. Lowering dark currents by decreasing pixel sizes and increasing quantum efficiencies by using polymer based semiconducting materials represent promising pathways and as such are currently under investigation. We envisage 1000-fold improvements in sensitivity for optimized polymer photodiodes.

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Paul Sullivan obtained a BSc in Chemistry from Imperial College London in 2002 and is currently a BP Solar funded PhD student studying novel organic photovoltaics and photodetectors.

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