One- and two-photon photocurrents from tunable organic microcavity photodiodes

R. Koeppe, J. G. Müller, J. M. Lupton,[a] and J. Feldmann
Photonics and Optoelectronics Group, Physics Department and CeNS, Ludwig-Maximilians-Universität München, Amalienstrasse 54, 80799 Munich, Germany

U. Scherf
FB Chemie, Universität Wuppertal, Gauss-Strasse 20, 42097 Wuppertal, Germany

U. Lemmer
Lichttechnisches Institut, Universität Karlsruhe, Kaiserstrasse 12, 76131 Karlsruhe, Germany

We have constructed multilayer thin-film organic microcavity photodiodes with the photoactive layer comprised of a spin-coated conjugated polymer and an evaporated C_{60} layer. The electrodes are designed as semitransparent mirrors which form a resonant cavity structure. The photocurrent spectra show distinct maxima at the optical resonances of the cavities, which are located up to 200 nm below the fundamental optical transition of the polymer. The design allows a simple tuning of the spectral response by varying the layer thickness. Microcavity photodiodes are also shown to be highly sensitive two-photon detectors, which exhibit a factor 500 improvement in the two-photon response compared to devices without photonic confinement. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1565710]

The emission as well as the photocurrent spectra of optoelectronic devices are determined by material properties as well as the boundary conditions of the optical field. Drastic changes in the spectra occur when the optically active material is embedded inside a microcavity, i.e., in an optical resonator with vertical dimensions of order the wavelength of light. Such devices have been proven to give major advantages for both light-emitting and detecting diodes. Microcavities have been utilized to improve the linewidth and the efficiency of inorganic and organic light-emitting devices (LEDs).[1–4] The spectral response of III–V semiconductor photodiodes has also been tuned by incorporating the active material into a microcavity.[5,6] Potential applications of these resonant cavity enhanced photodiodes are in the field of sensors and telecommunications. Organic semiconductors bear a large potential for applications in photodetectors[7] and solar cells.[8] Tailoring the photoresponse of organic photodiodes is a key issue for improvement of such devices. This has previously been achieved by chemically tuning the material parameters such as the energy of the fundamental optical transition. The role of electric field distribution in organic photodiodes was pointed out by Gattinger *et al.*[9] Recently, Narayan *et al.* demonstrated an organic photodiode exhibiting a narrow photoresponse by sandwiching a polythiophene layer between a gold contact and a dielectric Bragg stack mirror.[10] In this letter we show that the spectral response of an organic photodiode can be tuned and drastically enhanced by embedding a bilayer of a conjugated polymer and a fullerene into a microcavity resonator. Such organic microcavity photodetectors (OMPDs) are particularly useful for nonlinear optical applications, where the strength of the light–matter interaction squares with the magnitude of the optical field, which is in turn enhanced by the cavity struc-

ture. We show that the two-photon-induced photocurrent is enhanced by almost three orders of magnitude and allows subpicosecond temporal resolution.

Device fabrication was carried out under inert conditions in a N_2 glovebox. A glass substrate is first covered with a semitransparent silver layer of approximately 35 nm thickness by thermal evaporation. The film serves as a mirror and an electrode and exhibits reflectivities ranging from 0.7 at 450 nm to 0.9 at 650 nm. The photoactive layer consists of a methyl-substituted ladder-type poly(*p*-phenylene) (MeLPPP). It is spin coated on top of the silver electrode
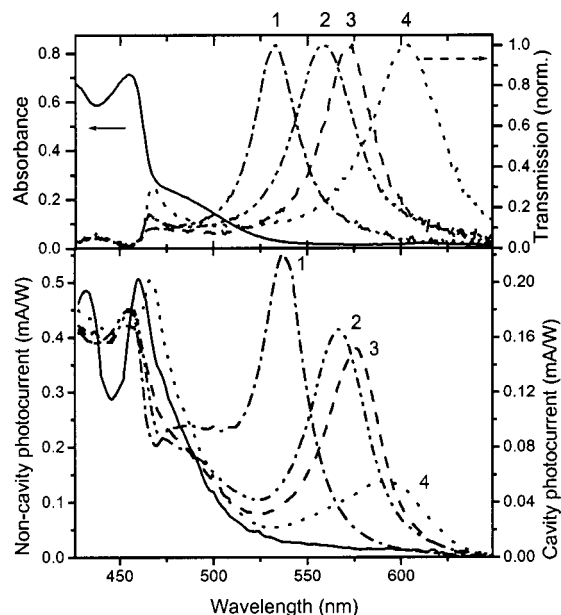

FIG. 1. Optical transmission (upper panel) and photocurrent (lower panel) spectra of four metal mirror OMPDs with different MeLPPP layer thicknesses (1: 142 nm, 2: 149 nm, 3: 153 nm, 4: 165 nm). The upper graph also shows the absorption spectrum of a MeLPPP/C_{60} bilayer (solid line), the lower panel gives the corresponding photocurrent spectrum (solid line).

[a] Author to whom correspondence should be addressed; electronic mail: john.lupton@physik.uni-muenchen.de
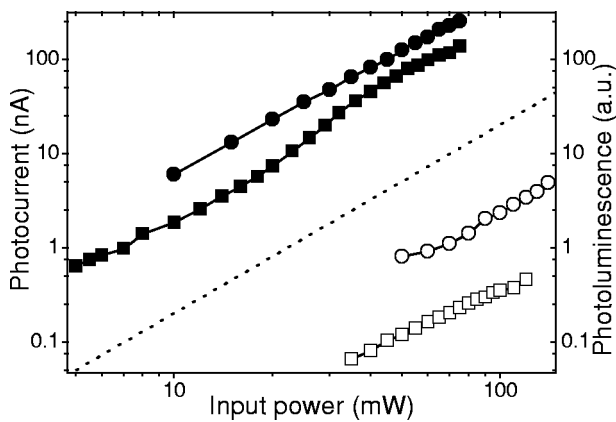
FIG. 2. Two-photon induced fluorescence (TPF, circles) and photocurrent (TPPC, squares) from diodes with (filled symbols) and without (open symbols) cavity confinement illuminated by a 1 kHz femtosecond laser at 780 nm. The dashed line indicates a quadratic intensity dependence.

from a toluene solution. While the quantum efficiency for charge carrier generation is rather limited in a single polymer layer it can be significantly increased by introducing an additional electron accepting layer. In our case we evaporate a thin film of approximately 100 nm thickness of C_{60} fullerene molecules which act as electron acceptors. Finally, a second silver film serving as the upper mirror and electrode is evaporated on top of the C_{60} layer, leading to the formation of a one-λ cavity in the visible with the first $\lambda/2$ resonance located in the infrared. We found that the electrical properties and the stability of the device could be dramatically enhanced by inserting a 2 nm layer of Al between the Ag layers and the polymer, which was done in the following experiments. The overall thickness of the organic bilayer is varied by changing the deposition parameters of the polymer layer. No external voltages were applied to the samples during measurement. The photocurrent spectra were measured by passing light from a 150 W tungsten lamp through a monochromator with a spectral resolution of <2 nm and focusing it onto the sample. Transmission spectra were taken using a UV–VIS spectrophotometer.

In Fig. 1 the transmission and photocurrent spectra of four different OMPDs with polymer layers of different thicknesses are summarized. As seen in the transmission data in the upper part of Fig. 1 the position of the cavity resonances is manifested by transmission peaks which vary systematically with the thickness of the organic semiconductor. By controlling the spin speed during polymer deposition it is possible to spectrally tune the resonance. For comparison, the absorption spectrum of the bilayer is shown on the left hand side of the upper panel. All our samples are designed such that the resonance wavelength is located below the fundamental absorption band of MeLPPP. At wavelengths shorter than 470 nm the absorption of MeLPPP sets in and suppresses the formation of higher-order transmission resonances.

The photocurrent spectra of the different OMPDs are shown in the lower part of Fig. 1. In the spectral range below 470 nm the typical photocurrent spectra of MeLPPP are observed. Neutral excitations are generated by direct $\pi-\pi^*$ transitions. A small fraction of these subsequently dissociate giving rise to a photocurrent. The main contribution to the photocurrent is expected to be generated at the interface be-

tween MeLPPP and the evaporated C_{60} layer, where charge transfer is highly efficient. In the spectral range of high absorption of MeLPPP the amount of photocurrent is basically the same for all samples. In a noncavity MeLPPP/C_{60} photodiode, the photocurrent decreases rapidly at wavelengths longer than 470 nm. This is indicated by the solid line in Fig. 1. The situation is completely different in cavity devices. Strong photocurrent peaks corresponding closely to the cavity resonances visible in the transmission are observed in all samples. It is important to note that the amplitude of these peaks located in the range of negligible absorption is comparable to the photocurrent in the spectral range of high absorption. The width of the peaks is mainly determined by the mirror reflectivity. Using silver mirrors with a thickness of 35 nm the resulting full width at half maximum (FWHM) is 30–40 nm, which corresponds to a Q factor of approximately 10. We attribute the very high photocurrent at the resonance wavelength to the strong field enhancement inside the cavity. This results in an increase in the probability of photon absorption, which means that charge carrier generation can occur even in the range of very low optical absorption. We note that the photocurrent resonances are slightly broadened to longer wavelengths with respect to the transmission resonances. We attribute this to a nonuniform photogeneration efficiency across the spectrum. We also note that the thickness of our polymer film is close to uniform and varies by 3 nm at most across the active region of the microcavity. This was established by moving the position of the incident light spot over the device but is also apparent from the narrow linewidth observed.

It is an important question which optically enhanced electronic transition is actually responsible for the subbandgap photocurrent. Most likely the weak absorption in the C_{60} layer gives the strongest contribution to the cavity induced photocurrent. Photoexcitations are generated in the C_{60} layer and are subsequently dissociated by a hole transfer at the interface to the MeLPPP layer. In addition, absorption below the fundamental $\pi-\pi^*$ transition might occur in the polymer due to the presence of red shifted defect sites[11,12] and anti-Stokes type absorption.[13] In agreement with our observations, numerical calculations indicate an enhancement of absorption at the cavity resonance of approximately 10 for our structures, which is consistent with the Q factor observed. A direct comparison between the cavity and noncavity photocurrents is difficult because the cavity device employs symmetrical electrodes whereas the resonance free device requires ITO and metal electrodes, which result in a change of the built-in field. The problem may be overcome by using ITO-coated Bragg reflectors as the lower electrodes.

While the cavity enhances the photocurrent substantially in the case of linear absorption much stronger effects are observed in the case of nonlinear two-photon absorption. Conjugated polymers are known to exhibit two photon induced fluorescence under certain conditions.[14,15] MeLPPP exhibits a large two-photon absorption cross section and has previously been used as a nonlinear medium in a number of experiments.[14–16] We modified the structure somewhat by using a distributed Bragg reflector (DBR) with a stop band of 100 nm width centered at 770 nm and a maximum reflectivity of 99.99% instead of the lower Ag mirror. The uppermost

Appl. Phys. Lett., Vol. 82, No. 16, 21 April 2003
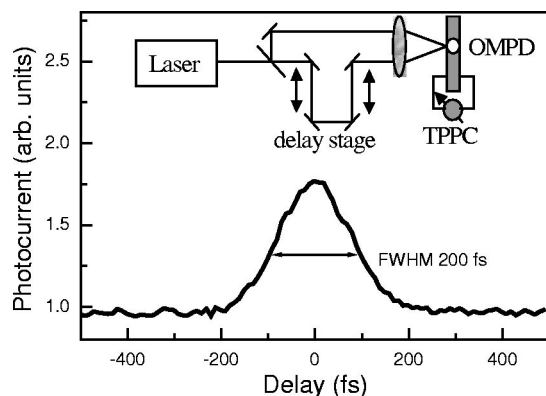
Koeppe *et al.*   2603

FIG. 3. Autocorrelation measurement of two-photon-induced photocurrent in dependence of the time delay between two incident laser beams of 120 fs pulse width. The inset shows the experimental setup.

layer of this dielectric mirror consisted of an ITO film serving as the lower electrode of the photodetector. In order to minimize linear absorption at the operational wavelength around 800 nm we omitted the fullerene layer. The much lower residual absorption at the cavity resonance in comparison to the one-photon devices results in an increase of the Q factor, which can be achieved by using a dielectric mirror. Reflectivity measurements and matrix transfer calculations indicate a Q factor for this structure of approximately 80. Excitation was performed using a regeneratively amplified femtosecond Ti:sapphire laser with a repetition rate of 1 kHz and a pulse duration of 120 fs. The excitation spot was not focused and had an area of 3 mm^2. Figure 2 compares the two-photon photocurrent (TPPC) and the two-photon fluorescence (TPF) of a cavity diode in the structure of Ag/MeLPPP/ITO/DBR and a simple Ag/MeLPPP/ITO sample in the absence of photonic confinement. As expected for two-photon excitation, all signals grow approximately quadratically with excitation intensity. Both the photocurrent output and the two-photon fluorescence are strongly enhanced by the cavity structure under illumination with femtosecond laser pulses at resonance at 780 nm. The dramatic increase by a factor of approximately 500 of the nonlinear response results from strong field enhancement in the OMPDs. We note that the increase in TPPC is substantially greater under optical confinement than the increase in TPF, which is a factor of approximately 200. This suggests that the field enhancement is particularly strong in the spatial region of charge separation. As our cavities are one-λ cavities, the optical standing wave has maxima in the vicinity of the electrodes rather than in the center of the device. Whereas the photocurrent generation is most efficient for excitation close to the electrodes, the fluorescence is least efficient there due to quenching processes. For this reason one would expect the cavity enhancement to be stronger for the TPPC than for the TPF. We note that previous results on inorganic two-photon photodiodes show substantially higher enhancement factors of up to 12 000.[17] This is, however, mainly due to the absence of an absorbing metal mirror and the use of two dielectric mirrors.

The strong TPPC allows the use of such nonlinear photodetectors for the characterization of ultrafast laser pulses without a need for additional nonlinear optical elements.[18] Figure 3 displays an autocorrelation measurement performed directly with the OMPD. Here, the laser pulses from a mode-locked Ti:sapphire laser operating at 80 MHz repetition rate a pulse width of 120 fs and energy of 60 pJ/pulse are fed into an autocorrelation setup. After passing the setup the two non-collinear beams are focused to a 500-μm-diam spot onto an OMPD with a resonance at the fundamental laser wavelength. The superlinear dependence of the two-photon photocurrent response on intensity is clearly manifested in the correlation peak, which arises when the two incident pulses overlap temporally. The width of the correlation peak of about 200 fs indicates only a very marginal broadening of the response, demonstrating the rather surprising result that ultrafast optical processes on the fs time scale may be detected and characterized with organic photodiodes.

In conclusion, we have fabricated organic microcavity photodiodes. The photoresponse in such devices shows a substantial enhancement in photocurrent in combination with spectrally narrow sensitivity. These findings can be attributed to the field enhancement at the cavity resonance wavelength. The resonance wavelength and the spectral response of such devices can be easily controlled by varying the organic semiconductor film thickness. This is expected to open new design routes to low-cost color detectors and spectrometers. Two-photon absorption is also strongly enhanced, making such organic microcavity photodiodes very interesting for nonlinear photodetector applications, which can serve, for example, as compact inexpensive autocorrelators or optical spectrum analyzers.

[1] E. F. Schubert, N. E. J. Hunt, M. Micovic, R. J. Malik, D. L. Sivco, A. Y. Cho, and G. J. Zydzik, Science **265**, 945 (1994).

[2] U. Lemmer, R. Hennig, W. Guss, A. Ochse, J. Pommerehne, R. Sander, A. Greiner, R. F. Mahrt, H. Bässler, J. Feldmann, and E. O. Göbel, Appl. Phys. Lett. **66**, 1301 (1995).

[3] N. Takada, T. Tsutsui, and S. Saito, Appl. Phys. Lett. **63**, 2032 (1993).

[4] A. Dodabalapur, L. J. Rothberg, R. H. Jordan, T. M. Miller, R. E. Slusher, and J. M. Phillips, J. Appl. Phys. **80**, 6954 (1996).

[5] M. S. Unlu and S. Strite, J. Appl. Phys. **78**, 607 (1995).

[6] M. Gokkavas, B. M. Onat, E. Ozbay, E. P. Ata, J. Xu, E. Towe, and M. S. Unlu, IEEE J. Quantum Electron. **35**, 208 (1999).

[7] Y. Gang, W. Jian, J. McElvain, and A. J. Heeger, Adv. Mater. **10**, 1431 (1998).

[8] C. J. Brabec, N. S. Sariciftci, and J. C. Hummelen, Adv. Funct. Mater. **11**, 15 (2001).

[9] P. Gattinger, H. Rengel, and D. Neher, J. Appl. Phys. **84**, 3731 (1998).

[10] Th. B. Singh, U. V. Waghmare, and K. S. Narayan, Appl. Phys. Lett. **80**, 1213 (2002).

[11] A. Köhler, J. Gruner, R. H. Friend, K. Müllen, and U. Scherf, Chem. Phys. Lett. **243**, 456 (1995).

[12] J. M. Lupton, Appl. Phys. Lett. **80**, 186 (2002).

[13] J. M. Lupton, Chem. Phys. Lett. **365**, 366 (2002).

[14] U. Lemmer, R. Fischer, J. Feldmann, R. F. Mahrt, J. Yang, A. Greiner, H. Bässler, E. O. Göbel, H. Heesel, and H. Kurz, Chem. Phys. Lett. **203**, 28 (1993).

[15] A. Hohenau, C. Cagran, G. Kranzelbinder, U. Scherf, and G. Leising, Adv. Mater. **13**, 1303 (2001).

[16] C. Bauer, H. Giessen, B. Schnabel, E. B. Kley, U. Scherf, and R. F. Mahrt, Adv. Mater. **14**, 673 (2002).

[17] H. Folliot, M. Lynch, A. L. Bradley, L. A. Dunbar, J. Hegarty, J. F. Donegan, L. P. Barry, J. S. Roberts, and G. Hill, Appl. Phys. Lett. **80**, 1328 (2002).

[18] L. P. Barry, P. G. Bollond, J. M. Dudley, J. D. Harvey, and R. Leonhardt, Electron. Lett. **32**, 1922 (1996).