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First demonstration of the use of very large Stokes shift Cycloparaphenylenes as promising organic luminophores for Transparent Luminescent Solar Concentrators

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Supplementary Information

1. General Experimental Details

HR mass spectra were acquired on an FT ICR mass spectrometer equipped with a 7T magnet. The samples were ionized using the MALDI ion source (15 laser shots were used for each scan). The mass spectra were calibrated externally, and a linear calibration was applied. The samples recorded in MALDI were prepared by mixing 10 μL of analyte in dichloromethane (1 mg/mL) with 10 μL of solution of dithranol or TCNQ (10 mg/mL in THF). All chemicals were reagent grade and were used without further purification. Tetrahydrofuran was dried by heating under reflux over sodium wire in the presence of benzophenone as the indicator[1] while dimethylformamide were dried by activated 3 Å molecular sieves. [2] When necessary the compounds were dried in vacuum over $CaCl_2$. Reaction temperatures were measured externally. Reactions were monitored by TLC silica gel plates (0.25 mm) and visualized by 254 nm UV light, or by spraying with H_2SO_4–$Ce(SO_4)_2$. NMR spectra were recorded on a 600 MHz spectrometer [600 (^1H) and 150 MHz (^{13}C)], 400 MHz spectrometer [400 (^1H) and 100 MHz (^{13}C)] or 300 MHz spectrometer [300 (^1H) and 75 MHz (^{13}C)], spectrometer. Chemical shifts are reported relative to the residual solvent peak.[3]

The derivatives **1** and **2** have been synthesized according to literature procedures.[4] The reduction of the derivative **1** and **2** has been performed through a slightly modified procedure with respect to that previously reported by Jasti and co-workers.[4] The spectroscopic ^1H and ^{13}C NMR data of all the compunds here synthesized are in accord with those reported in literature.[4]

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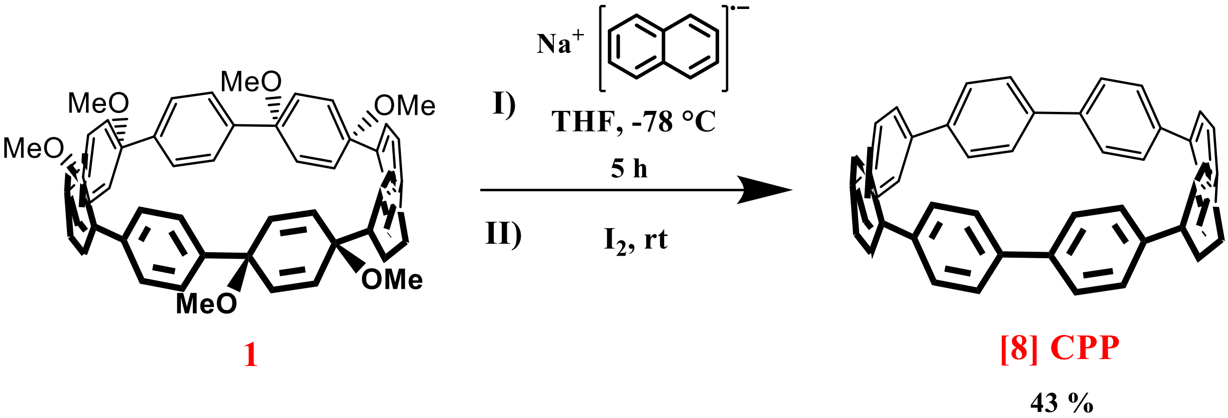
[1] B. S. Furniss, A. J. Hannaford, P. W. G. Smith, A. R. Tatchell in *Vogel's Textbook of Practical Organic Chemistry, 5th ed.*; Pearson: Harlow, **1989** and references cited therein.

[2] D. B. G. Williams and M. Lawton, *J. Org. Chem*. 2010, **75**, 8351.

[3] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B.M. Stoltz, J.E. Bercaw, K.I. Goldberg, *Organometallics* 2010, **29**, 2176.

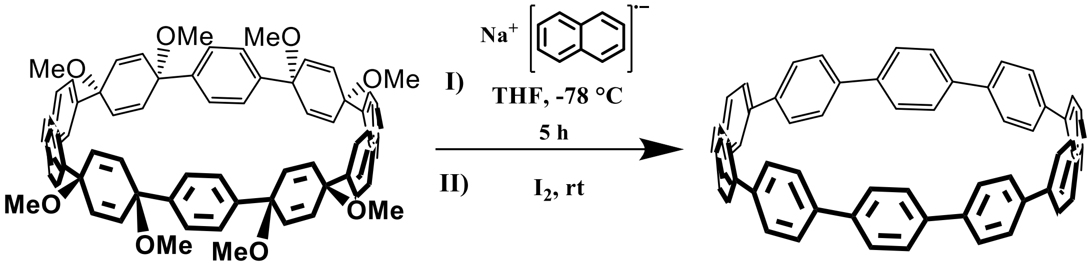
[4] J. Xia, J. W. Bacon, R. Jasti, *Chem. Sci.* 2012, **3**, 3018

a. Synthesis of [8]CPP



Macrocycle **1** (530 mg, 0.67 mmol) was dissolved in 47 mL of dry THF, under N_2, and the solution was degassed through the freeze/pump/thaw technique and cooled to −78 °C. Then, a solution of sodium naphthalenide freshly prepared (5.5 mL, 5.5 mmol, 1.0 M in dry THF), was added and the reaction mixture was stirred for 5 h at − 78 °C. Then, a I_2 solution was added (4.6 mL of a 1.0 M in THF) and the reaction mixture was warmed at room temperature. Then, an aqueous saturated solution of sodium thiosulfate (20 mL) and CH_2Cl_2 (30 mL) was added, and the reaction mixture was stirred for 15 min. The organic layer was extracted, and the aqueous phase was washed with CH_2Cl_2 (3 × 20 mL). Finally, the combined organic layers were washed with a saturated brine solution (60 mL) and dried over sodium sulfate and filtered. The solvent was removed under reduced pressure, and the crude product was purified by chromatography column on silica gel under nitrogen flow (petroleum ether/ CH_2Cl_2 = 8:2), to give **[8]CPP** as a yellow solid in 42 % yield (170 mg). HRMS (MALDI) *m*/*z* $[M]^+$ calcd for $C_{48}H_{32}$, 608.2504; found, 608.2524. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 7.48 (s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 127.44, 137.63.

b. Synthesis of [10]CPP



2

[10] CPP

77 %

Macrocycle **2** (120 mg, 0.12 mmol) was dissolved in 10 mL of dry THF, under N_2, and the solution was degassed through the freeze/pump/thaw technique and cooled to −78 °C. Subsequently, a solution of sodium naphthalenide freshly prepared (1.5 mL, 1.5 mmol, 1.0 M in dry THF), was added and the reaction mixture was stirred for 5 h at −78 °C. Then, a I_2 solution was added (1.3 mL of a 1.0 M in THF) and the reaction mixture was warmed at room temperature. Then, a saturated solution of sodium thiosulfate (10 mL) and CH_2Cl_2 (30 mL) was added, and the reaction mixture was stirred for 15 min. The organic layer was extracted, and the aqueous phase was washed with CH_2Cl_2 (3 × 15 mL). Finally, the combined organic layers were washed with a saturated brine solution (40 mL) and dried over sodium sulfate and filtered. The solvent was removed under reduced pressure, and the crude product was purified by chromatography column on silica gel under nitrogen flow (hexane/ CH_2Cl_2 = 9:1), to give **[10]CPP** as a yellow solid in 77 % yield (70 mg). HRMS (MALDI) *m/z* $[M]^+$ calcd for $C_{60}H_{40}$, 760.3130; found, 760.3150. ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 7.56 (s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 127.34, 138.14.

c. Copies of ^{1}H NMR Spectra

^{1}H NMR of [8]CPP.

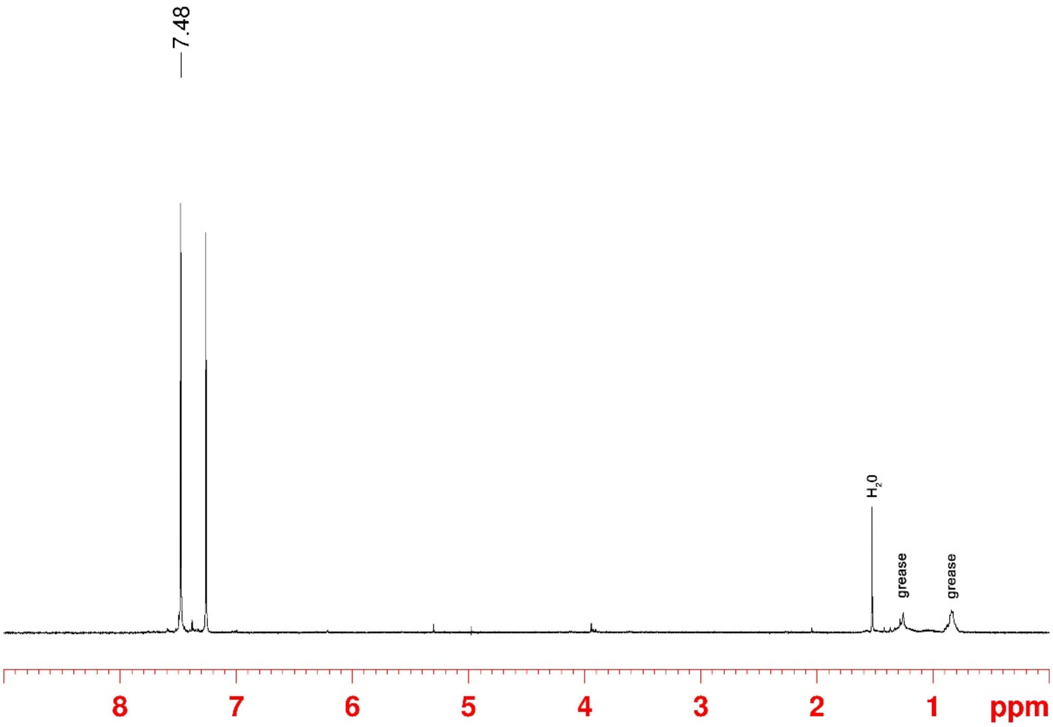


Figure 1: ^{1}H NMR spectrum of [8]CPP ($CDCl_3$, 400 MHz, 298 K).

^{1}H NMR of [10]CPP.

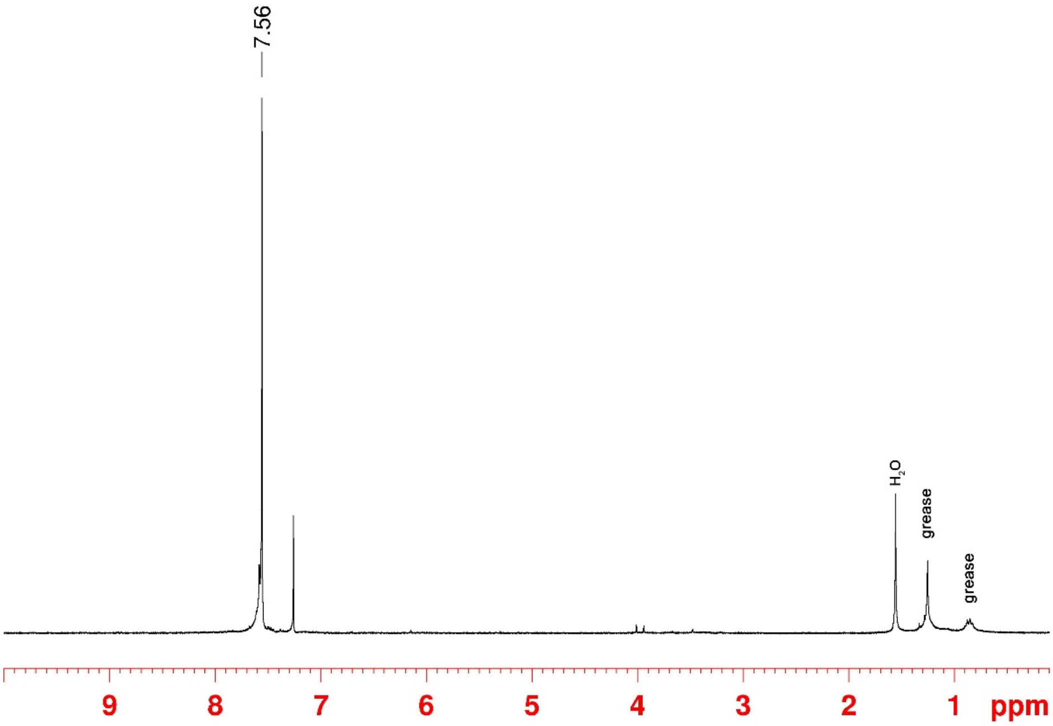


Figure 2: ^{1}H NMR spectrum of [10]CPP ($CDCl_3$, 300 MHz, 298 K).

2. Details of the slab preparation

Thermal route.

In a typical procedure for the preparation of a 0.1 % by weight slab, 100 mg of AIBN were dissolved in 100 ml of freshly distilled MMA. The solution was placed in a beaker and slowly heated on a hot plate until the temperature of 80 °C was reached. This temperature was maintained for 2 minutes, during which time viscosity increased substantially. The solution was immediately transferred in an ice bath and cooled at 20°C. A solution of [n]CPP (160 mg) in freshly distilled MMA (60 ml) was added along with 150 mg of lauryl peroxide. The viscous syrup thus obtained was poured in a mould of 3 mm thickness and 100 cm^2 area and heated in a water bath at 56°C for 48 h. At the end of this thermal treatment the syrup turns into a solid slab that is further cured at 95°C for 24 h. After cooling, the slab can be easily separated by the glass mould, cutted and polished for optical measurements.

Photochemical route.

To the syrup obtained according to the chemical route, a solution of Irgacure 651 and [n]CPP in distilled MMA was added so that the concentration of both compounds was 0.1 % wt with respect to the total MMA mass. The viscous solution was poured in a mold put between two 365 nm UV lamps and irradiated until it generates heat (10 min). Polymerization was than terminated at 95 °C for 24 h.

3. Figure S1. Comparison between the absorption spectra of chemically and photochemically polymerized slabs containing [8]CPP.

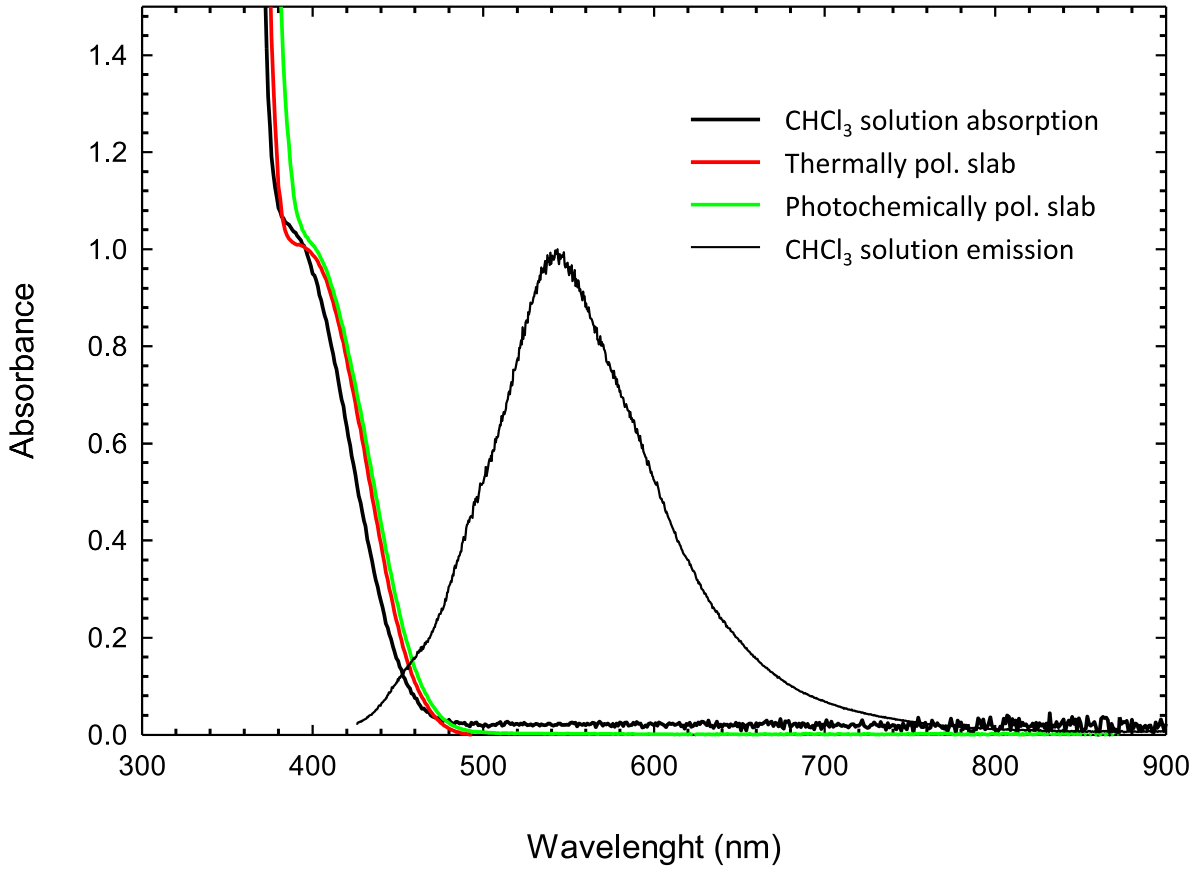


Figure S1. Comparison between the absorption spectra of a [8]CPP $CHCl_3$ solution (black tick line), a thermally polymerized slab (red line) a photochemically polymerized slab (green line). The thin black line shows the emission spectrum of the $CHCl_3$ solution.

4. Figure S2. Comparison of the emission profile in thermally and photochemically polymerized PMMA slabs containing [8]CPP.

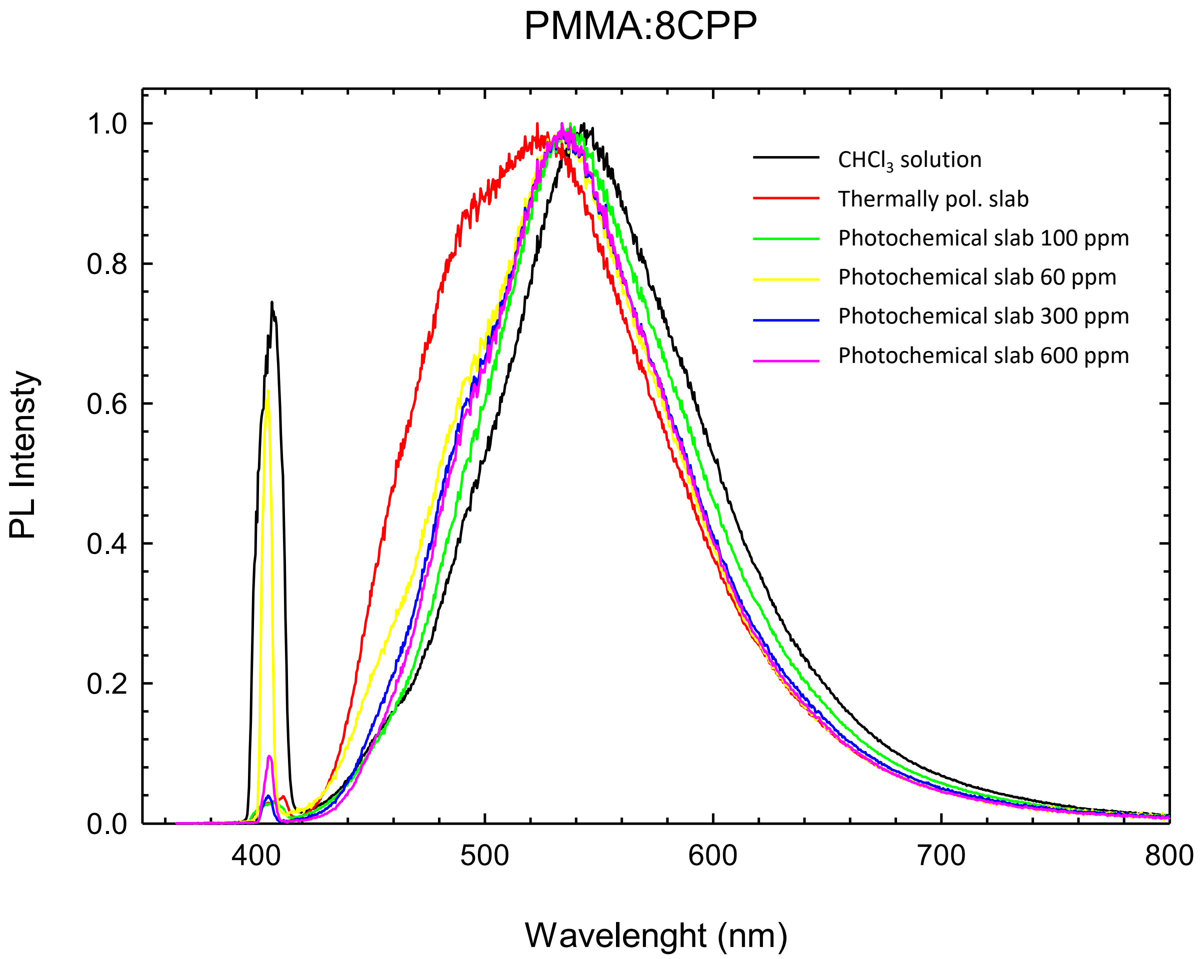


Figure S2. Comparison of the emission profile (excitation at 405 nm) of a CHCl3 solution of [8]CPP (black line, of a thermally polymerized slab at 600 ppm [8]CPP concentration (red line), a 60 ppm (yellow line) 100 ppm (green line) 300 ppm (blue line) and 600 ppm (purple line) photochemically polymerized slab.

5. Figure S3. Characterization of the photostability of [8]CPP and [10]CPP containing slabs.

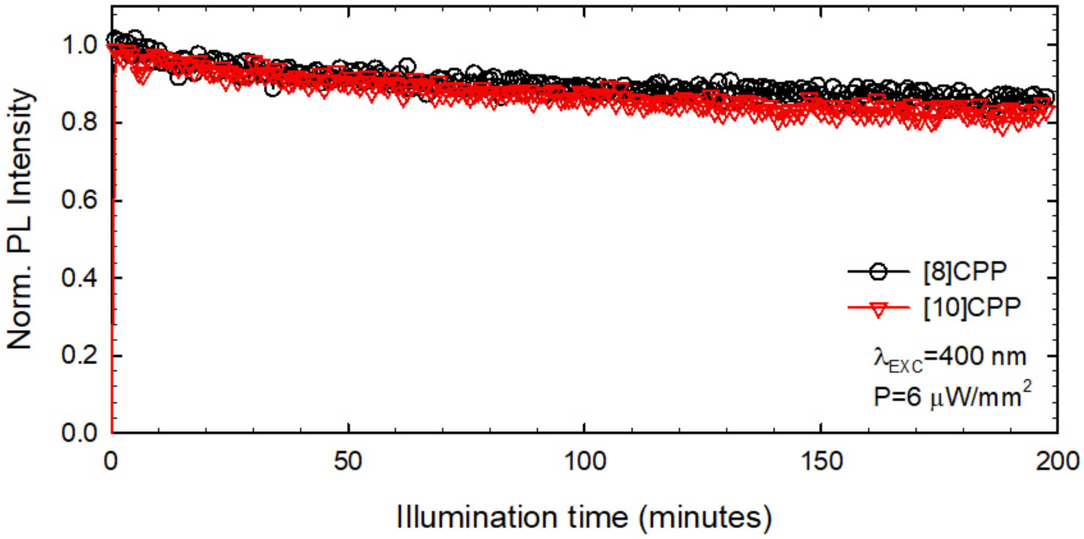


Figure S3. Normalized PL intensity of LSCs based on [8]CPP and [10]CPP under continuous illumination with UV light at 400 nm. The illumination density is 6microW/mm2, corresponding to over five times the solar irradiation at 400 nm in 1.5AMG conditions.

6. Photoluminescence measurement

The photo physical characterization of the LSCs were performed illuminating a spot of the larger surface of the slab with a titanium-sapphire. The light was waveguided through an optic fiber, varying the distance to the edge. The laser power output from the edge was measured using a CCD PHIR Nova PD300-3 photodiode. The setup scheme is reported in the figure.