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π -Conjugated polyHIPEs as highly efficient and reusable heterogeneous photosensitizers†

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π -Conjugated microporous polyHIPEs are synthesized via Suzuki cross-coupling. The polymeric backbone consists of electron donor and acceptor moieties with suitable energetic characteristics to promote the efficient photosensitizing ability for the activation of singlet oxygen, showing extraordinarily high stability. The reaction can be carried out in a continuous flow reaction set-up, realizing complete conversion of α -terpinene into ascaridole.

Polymerized high internal phase emulsions (polyHIPEs) are a relatively new class of porous lightweight organic materials with an appealing prospect to be used as catalysts,¹ supports in organic synthesis² or as filtration and separation media.^{3,4} In principle, a HIPE is formed by adding a disperse droplet phase (usually aqueous) to the mechanically agitated continuous phase containing all monomeric reactants, reagents and a surfactant. The continuous phase is then polymerized (*e.g.* via UV, thermal, redox or catalytic curing) and, after the removal of the droplets, a monolithic material with well-defined interconnected pores is achieved.^{5–8}

Combination of this large scale porosity with the very high specific surface area of a π -conjugated microporous polymer (CMP) or framework offers the opportunity to synthetically tailor the physical behavior and electronic properties of the polymer according to a targeted application.⁹ We will illustrate that conjugated polyHIPEs are prospective candidates for heterogeneous photocatalysis due to the possibility of tuning their morphology and tailoring the energy levels and absorption wavelengths in the visible light region. Moreover, polyHIPEs are cross-linked, insoluble in common solvents, have optimized transport and flow properties, and therefore can be easily engulfed by the reaction mixture, ideally in a continuous flow and without the need for catalyst separation after reaction.

From our previous findings,^{10,11} a well-defined combination of a weak electron donor and a strong electron acceptor may lead to

an effective exciton localization, slow radiative recombination of the generated charge pair, but also encourage a high yield of intersystem crossing to the triplet state of the excited polymer framework. Additionally, if the absolute positions of HOMO and LUMO are chosen to enable the sufficient oxidation stability of the framework as well as reactivity, this can result in an appropriate energetic state for photocatalytic generation of singlet oxygen.

Unlike most natural compounds, molecular oxygen has triplet multiplicity in the ground state and an excited singlet state lying 95 kJ mol⁻¹ (corresponding to a 1250 nm photon) higher.¹¹ The most common and widely used generation of singlet oxygen is based on photosensitizers.^{12,13} This simple method requires only an oxygen source, light of an appropriate wavelength and a photosensitizer possessing an energetically suitable excited triplet state. By absorption of light, the photosensitizer excites to its singlet state (S) followed through subsequent intersystem crossing by population of a triplet state (T). The excited sensitizer can transfer energy and spin to the ground state triplet oxygen, thus forming the excited singlet oxygen.^{12,13} Singlet oxygen has a lifetime of less than 1 s in solution and can be rapidly deactivated back to the ground state *via* physical or chemical quenching. Given its strong electrophilic and oxidizing character, it has been widely used as a versatile synthetic reagent in range of applications including organic synthesis,¹⁴ environmental water treatment¹⁵ or photodynamic therapy of cancer.¹⁶

Most commonly used photosensitizers include dyes such as rose bengal, eosin, methylene blue, or biocompatible porphyrin or phthalocyanine derivatives.¹³ These materials are usually used in a homogeneous manner, which creates an additional issue of subsequent isolation from the system or even proliferation in biological systems. Compared to this conventional homogenous approach, the use of heterogeneous photosensitizers in principal would offer several advantages in practical applications. They can be easily isolated, recovered and recycled when applied, for instance, in water purification systems. Moreover, due to their insolubility, they can be used in a variety of solvents and subsequently filtered off from the reaction mixture, thus establishing an unparalleled versatility and simplicity in terms of chemical synthesis and purification procedures.¹³

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† Electronic supplementary information (ESI) available: Synthetic routes, elemental analysis, FTIR spectra, CD MAS ¹³C NMR in solid state, TGA analysis of **B-FL**₃, **B-BT-FL**₂ and **B-BT₂-FL**, experimental details of the singlet oxygen generation set-up, and the ¹H NMR spectrum and UV absorption of BT-FL. See DOI: 10.1039/c3cc45597a

In this work, we will employ an electron system consisting of a strong electron-withdrawing moiety benzothiadiazole (BT) and weak electron-donating moieties, here benzene (B) and fluorene (FL), within a conjugated backbone. Based on its small band gap, high absorption coefficient and suitable chemical stability, benzothiadiazole has been utilized in optoelectronic materials such as low-band-gap polymers,^{17–20} non-fullerene acceptors,²¹ or n-type field effect transistors.²² Benzene can be easily functionalized in different positions by a wide range of substituents, and many of the building blocks are commercially available at low cost.

This layout of photocatalytic activity of the novel fully conjugated porous polymers is then coupled to HIPE polymerization (CMP-HIPES) for the microscale design. The synthesis was carried out *via* palladium-catalyzed Suzuki cross-coupling, where 1,3,5-tribromobenzene (B) was used as a cross-linker reacting with different ratios of boronic ester derivatives of benzothiadiazole (BT) and fluorene (FL). The resulting polymers are expected to have statistically random distributions of BT and FL linkers due to the unequal reactivities of these moieties. From the analysis provided, the resulting polymers are structurally in good agreement with the ratio of the starting materials. The exact procedures of the synthesis and characterization of the polymers are described in the ESI† (Scheme S1, Fig. S1–S6 and Tables S1–S3). It is noted that to produce a stable emulsion resulting in monolithic CMP-HIPES, alkylated monomers such as the FL unit employed need to be present. Attempts to produce the **B-BT₃** HIPE in the absence of FL units were not successful.

The SEM images and optical photographs of the resulting polymer scaffolds are presented in Fig. 1, proving that highly macroporous monolithic structures were formed.

This is in agreement with the BET results, which show surface areas of 35–50 m² g⁻¹, which are within the range of previously reported polyHIPE materials.^{2,5} In addition, the pore distribution analysis confirms the presence of micropores within the structures proving the hierarchical morphology of the scaffold (ESI,† Fig. S6). Moreover, owing to the highly cross-linked and rigid aromatic character of the polymeric backbone, very stable monolithic architectures are achieved. These monoliths are, after drying, in all cases in the range of 1 cm height, with densities ranging from 50 to 80 mg cm⁻³.

Fluorescence spectra were recorded in the solid state using a quartz sample chamber (ESI,† Fig. S1). The emission of the

polymers containing the BT unit (**B-BT-FL₂** and **B-BT₂-FL**) is strongly red-shifted due to its strong electron withdrawing character, which results in a lower LUMO level and narrower band gaps. The same trend is also observed in UV reflection spectra (ESI,† Fig. S2), also recorded in the solid state.

Two different methods were used to investigate the feasibility of heterogeneous photocatalysis to be executed by the CMP HIPES. The first technique was based on a classical, stirred reaction set-up. Small pieces of the porous CMP-HIPES together with a solution of α -terpinene were placed in a reaction vessel, which was irradiated with blue light at 420 nm, while oxygen gas was bubbled through it (reaction condition: 5 mg of CMP-HIPES, 10 mL of 0.1 M α -terpinene solution in CHCl₃, oxygen flow rate = 10 mL min⁻¹). The well-known transformation of α -terpinene *via in situ* generated singlet oxygen yields ascaridole.

Reaction progress was followed by ¹H NMR, and the conversion calculated from the ratio of peaks assigned to starting material and product (ESI,† Fig. S8).¹⁰ 50% conversion was observed after 6 h when **B-FL₃** was used. In comparison, complete conversions were achieved by using **B-BT-FL₂** and **B-BT₂-FL** after 60 and 30 min, respectively (Fig. 2).

This observation suggests that incorporation of the strong electron accepting BT unit into the polymer backbone favours the triplet state under excitation, which is essential for the photosensitized generation of singlet oxygen. The fact that **B-BT₂-FL** facilitated faster reaction could be interpreted as a stronger inter-crossing process due to higher BT content within the conjugated system resulting in a more stable triplet state of the charge pair under excitation. However, further photophysical measurements are required to confirm this hypothesis. The second method utilized a reaction in a continuous flow system as depicted in Fig. 3a (and ESI,† Fig. S7). The continuous flow set-up offers several advantages over conventional reaction methods, which include the opportunity to scale-up *via* an increase of the reaction time rather than the size of the reaction vessel, or the possibility of precise control of the reaction parameters (temperature, contact time, mass transfer or mixing).¹⁴ In the particular case of heterogeneous photocatalysis, light can more efficiently penetrate through thin tubing rather than bulk solution in a flask, giving rise to more efficient singlet oxygen generation. Moreover, the polymeric catalyst can be permanently placed in one part of the whole system (*e.g.* fritted glass column) whilst the solution flows through it; this can dramatically ease up isolation steps.

The best performing polymer from the previous experiments (**B-BT₂-FL**) was used. Small pieces of the **B-BT₂-FL** monolith (10 mg),

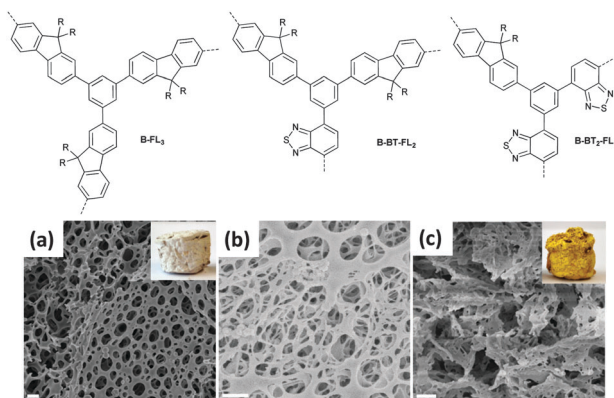


Fig. 1 Idealized structures and SEM images of (a) **B-FL₃**, (b) **B-BT-FL₂** (c) **B-BT₂-FL**, scale bar = 1 µm. Insets – photographs of corresponding CMP-HIPE monoliths.

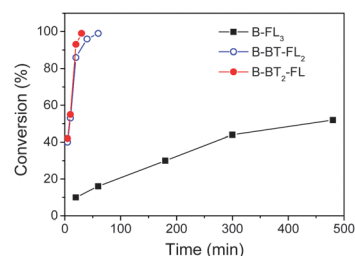


Fig. 2 Conversion of ascaridole from the oxidation of α -terpinene using the CMP-HIPES as heterogeneous photocatalysts.

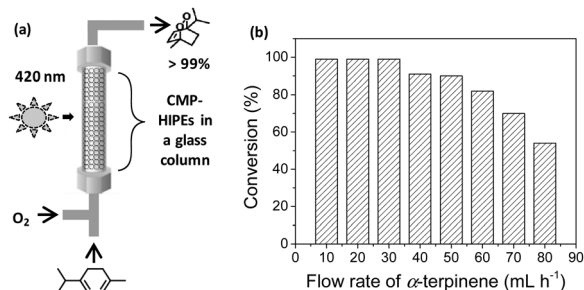


Fig. 3 (a) Schematic presentation of the continuous flow set-up for photo-oxidation of α -terpinene; (b) ascaridole conversions at different flow rates of α -terpinene solution.

were placed into a photoreactor consisting of a glass column ($r = 0.35$ cm, $L = 7$ cm) and FEP (fluorinated ethylene propylene) tubing. A solution of α -terpinene (0.1 M in 10 mL CHCl_3) was mixed with oxygen and pumped through the reactor which was irradiated with blue light at 420 nm (see ESI† Fig. S7). Full conversion to ascaridole was observed.

To demonstrate the lifetime or reusability of the CMP-HIPES, 10 repeating experiments were carried out using the same batch of **B-BT₂-FL** at constant flow rates of oxygen (5 mL min⁻¹) and α -terpinene solution (20 mL h⁻¹). The perpetuated quantitative conversion of ascaridole in all experiments proves the exceptional photoactivity and photostability of **B-BT₂-FL** (ESI† Fig. S8).

The reaction kinetics were investigated by varying the flow rates of the α -terpinene solution, whilst keeping the oxygen flow constant (5 mL min⁻¹). Fig. 3b indicates that complete conversion to ascaridole is observed only up to rates of 30 mL h⁻¹, up to which a sufficient contact time for the singlet oxygen–diene reaction was provided. Increasing the flow rate of the α -terpinene solution decreases the conversion to 52% of product at 80 mL h⁻¹. This translates into an overall reaction time, under the given set of conditions, of about 2 minutes.

To determine the amount of generated singlet oxygen using **B-BT₂-FL** as the photosensitizer, a concentrated α -terpinene solution (0.33 M and 20 mL h⁻¹) was injected into the glass column along with oxygen (5 mL min⁻¹). In this case, a conversion of 23% of ascaridole was detected and therefore the calculated minimum amount of produced singlet oxygen by 1 mg of **B-BT₂-FL** equals 0.0025 mmol min⁻¹.

As a control experiment, a linear BT–FL alternating polymer (BT–FL)²³ was synthesized (see ESI† for experimental details, Fig. S10–S12) and tested as a homogeneous photocatalyst. Complete conversion of ascaridole was determined after 20 minutes using the bulk reaction set up. This supports a molecular layout consisting of BT and FL units satisfying the required parameters for stability and efficient triplet transfer. In addition, a direct comparison of the molecular homogeneous catalyst with the insoluble microporous CMP-HIPES architecture indeed shows that heterogenization comes with practically no loss in reaction speed, but enables the reaction to proceed under heterogeneous conditions and to be used in flow reactors, without the need for catalyst separation.

In conclusion, a series of fully π -conjugated microporous polymers with polyHIPES macrostructure were prepared *via* Suzuki cross-coupling. This allows for π -conjugated microporous materials to be combined with a favorable macro architecture in order to create functional materials for a variety of applications. To the best of our knowledge this is the first time that fully conjugated polyHIPES are reported, and that a Suzuki coupling could be performed under such conditions. Different combinations of electron donor and acceptor moieties were incorporated into the polymer backbones in order to investigate their influence on photocatalytic activity for singlet oxygen generation, as monitored by an *in situ* reaction with α -terpinene. The pure electron donor system (**B-FL₃**) showed low photocatalytic activity, whereas incorporation of strong electron acceptor units into the polymeric chain (**B-BT-FL₂** and **B-BT₂-FL**) demonstrated dramatic improvement of the photocatalytic activities. **B-BT₂-FL** in particular proved to be a stable, reusable and efficient photocatalyst, facilitating full conversion of ascaridole in a continuous flow reaction set-up with overall contact times as low as 2 min. CMP-HIPES, in our opinion, represent a new promising family of recyclable heterogeneous photocatalysts, which will significantly simplify the handling and purification of sensitive reactions.

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