



Conjugated Polymers Hot Paper

How to cite:

International Edition: doi.org/10.1002/anie.202010795 German Edition: doi.org/10.1002/ange.202010795

# **Click-Functionalization of a Poly(Tetrazine)-co-Fluorene-Conjugated Polymer with a Series of** *trans***-Cyclooctene Derivatives**

Vladimir Kardelis, Maria M. Denk, and Alex Adronov\*

Abstract: A soluble poly(tetrazine) polymer was prepared via Suzuki polycondensation of 3,6-bis(5-bromofuran-2-yl)-1,2,4,5-tetrazine and a fluorene diboronate derivative. It can undergo efficient and quantitative post-polymerization inverse-electron-demand Diels-Alder click reactions with a variety of trans-cyclooctene (TCO) derivatives. The resulting polymers were oxidized to convert dihydropyridazine rings into pyridazines. The absorption spectra of the product polymers, both before and after oxidation, showed hypsochromic shifts that correlated with steric hindrance of the appended side chains. They also exhibited a significantly enhanced fluorescence intensity relative to the original poly(tetrazine). While gel-permeation chromatography indicated that the product polymers exhibited longer retention times, NMR end-group analysis showed that the polymers retained relatively constant degrees of polymerization. Graft copolymers were easily prepared via reaction with TCO-functionalized poly(ethylene glycol) chains and a cross-linked foam was produced by reacting the poly(tetrazine) with a bis-TCO crosslinker.

# Introduction

Since their discovery, conjugated polymers have played an increasingly important role in numerous disruptive technologies. The wide array of structures that constitute the polymer backbone allows their optimization for applications that include lighting and displays,<sup>[1]</sup> energy generation and storage,<sup>[2,3]</sup> sensors,<sup>[4,5]</sup> field-effect transistors,<sup>[6,7]</sup> as well as information storage and computing.<sup>[8]</sup> A variety of conjugated polymer properties can be modified by varying polymer structure, including band gap, HOMO and LUMO levels, extinction coefficient, quantum yield, conductivity, and solubility.<sup>[9-14]</sup> However, modification of polymer properties typically requires the preparation of new polymer structures, which are prepared via de novo synthesis incorporating new monomers.<sup>[12]</sup> When developing polymers for new applications, it is often necessary to prepare libraries of homologous polymers that exhibit only small changes from one to another. Such small changes are difficult to achieve when carrying out polymerizations with different monomers, as control over molecular weight and dispersity in conjugated polymers remains a challenge in all but a few specialized polymerization methods.<sup>[15–21]</sup> These factors greatly impact the resultant polymer morphologies and other physical properties, such as solubility. Thus, post-polymerization functionalization has been widely considered. Although modification of a preformed conjugated polymer can be routinely achieved through the chemistry of side-chains, quantitative changes to the conjugated backbone are much more difficult. Only a few examples of efficient modification of a conjugated polymer backbone have been published, including Cu(OTf)<sub>2</sub>catalyzed benzannulation of phenylene ethynylenes,<sup>[22]</sup> and nucleophilic aromatic substitution on aryl fluoride derivatives of benzothiadiazole monomer units.<sup>[23]</sup>

In previous work, we have shown that post-polymerization functionalization of a dibenzocyclooctyne (DIBO)containing conjugated polymer is possible via strain-promoted alkyne-azide cycloaddition (SPAAC).[24-26] Not only is SPAAC functionalization rapid (2<sup>nd</sup> order rate constant of  $0.031 \text{ M}^{-1} \text{s}^{-1}$ ), but the reaction was shown to be efficient enough to quantitatively functionalize the polymer backbone with 24 kDa polystyrene azide, resulting in a graft copolymer having a number average molecular weight (M<sub>n</sub>) exceeding 800 kDa.<sup>[24]</sup> Though a versatile polymer, the DIBO-containing polyimine is plagued with poor hydrolytic stability,<sup>[27]</sup> and the multi-step synthesis to the monomer is prohibitive to its applications (six steps; overall yield of 7%). In addition, classic metal-mediated cross-coupling conditions cannot be used to polymerize the cyclooctyne monomer, as it rapidly generates metallocycles with the strained triple bond. Furthermore, upon SPAAC coupling with azide derivatives, we found that the polymer backbone adopts a severely kinked conformation, which detracts from any favourable optoelectronic properties that the parent polymer exhibits.

Rather than working with strained cyclooctynes as the reactive moiety, which precludes classic transition metalcatalyzed cross coupling polymerizations, we decided to introduce the *s*-tetrazine moiety into the polymer backbone. 1,2,4,5-Tetrazines undergo inverse-electron-demand Diels– Alder (IEDDA) reactions with various cyclooctenes, cyclooctynes, and norbornenes with  $2^{nd}$  order rate constants ranging from 1 to  $10^6 M^{-1} s^{-1}$ .<sup>[28]</sup> In addition to their fast reaction rates and bioorthogonal reactivity, 1,2,4,5-tetrazines are relatively simple to synthesize, often in 1–2 steps from commercially available starting materials. Furthermore, they tolerate Suzuki conditions, which facilitate the formation of high molecular weight conjugated polymers. Herein, we describe a convenient method for synthesizing a conjugated *s*-tetrazine-containing polymer and its resultant series of

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 <sup>[\*]</sup> V. Kardelis, M. M. Denk, A. Adronov
 Department of Chemistry and Chemical Biology and the Brockhouse
 Institute for Materials Research, McMaster University
 1280 Main Street West, Hamilton, Ontario, L8S 4M1 (Canada)
 E-mail: adronov@mcmaster.ca

Supporting information and the ORCID identification number(s) for
 the author(s) of this article can be found under: https://doi.org/10.1002/anie.202010795.



Scheme 1. Synthesis of the s-tetrazine-Br<sub>2</sub> monomer (a), and synthesis of the s-tetrazine containing polymer P1 (b).

cycloadduct polymers via post-polymerization IEDDA chemistry.

## **Results and Discussion**

#### Preparation of s-Tetrazine-Containing Polymer (P1)

The tetrazine monomer 2 was synthesized according to a literature procedure,<sup>[29]</sup> wherein commercially available 2furonitrile undergoes a modified Pinner reaction with hydrazine hydrate followed by an oxidation with isoamyl nitrite to generate the s-tetrazine 1 (Scheme 1a). This tetrazine was then doubly brominated using N-bromosuccinimide to yield the desired s-tetrazine-Br<sub>2</sub> monomer 2 in a modest 31 % yield over the two steps. Monomer 2 was readily copolymerized with a previously synthesized fluorene bis(pinacolato)boronate ester comonomer 3<sup>[30]</sup> via Suzuki polycondensation under mild conditions (50°C for 15 minutes) to yield the progenitor s-tetrazine-containing polymer P1 (Scheme 1b). The Suzuki reaction produced a polymer with a number average molecular weight of 38.8 kDa and a dispersity (D) of 1.6, as determined by gel permeation chromatography (GPC). To provide a functional NMR handle that could be used to corroborate the GPC data for P1 and all subsequent cycloadduct polymers, growing polymer chains were end-capped by adding *p*-anisole pinacolato boronate ester 4 and allowing the mixture to stir for 30 min. Anisole was used because the phenyl methoxy group provides a distinct <sup>1</sup>H-NMR resonance at  $\approx$  3.85 ppm, which does not overlap with any other signals corresponding to the polymer chain (See Supporting Information, Figure S26). Based on the integration of this signal, the degree of polymerization (DP) for P1 was found to be 44, which corresponds to an  $M_n$  (NMR) of 36.3 kDa, in excellent agreement with the GPC data. The reactive, conjugated polymer P1 was further characterized via UV/Vis, and infrared (IR) spectroscopy, as well as by thermogravimetric analysis (TGA), with details provided in the Supporting Information. The TGA thermogram of this polymer showed two distinct decompositions, including a 7% mass loss at  $\approx$  280 °C corresponding to the loss of N<sub>2</sub>, and a 78 % mass loss at  $\approx 400$  °C corresponding to the loss of the hexadecyl sidechains of the fluorenyl monomer (Figure S62).

## Having prepared the reactive polymer **P1**, we set out to investigate its ability to undergo inverse electron demand Diels-Alder (IEDDA) reactions with a small library of trans cyclooctene (TCO) derivatives. This began with the preparation of rel-(1R, 4E, pR)-Cyclooct-4-enol (5) from the corresponding (Z)-cyclooct-4-enol following the procedure of Fox and co-workers.<sup>[31]</sup> The TCO derivatives were synthesized via activation of 5 using nitrophenyl chloroformate to form carbonate 6, followed by the substitution of the activated enol with a series of amines to yield carbamates **7a-f** (Scheme 2). Aliphatic and benzylic amines were used due to their relatively high nucleophilicity, allowing the reactions to be performed at room temperature, thereby minimizing the risk of thermal reisomerization to the (Z)-cyclooctenol. All coupling reactions with the small molecule derivatives proceeded to high conversion, allowing isolation of the desired products (7a-e) in excellent yield ( $\approx 90\%$ ) after chromatographic purification. In addition, a 5 kDa a-methoxy ω-amino poly(ethylene glycol) (PEG-NH<sub>2</sub>) was appended in order to investigate the formation of a graft copolymer via IEDDA. The resulting PEG-TCO derivative (7 f) was isolated in 74% yield after precipitation.

**Preparation of TCO Derivatives** 



Scheme 2. Preparation of a library of *trans*-cyclooctene (TCO) derivatives.

a)

b)

#### Post-Polymerization IEDDA Onto P1

The IEDDA reactions between P1 and the TCO derivatives 5 and 7a-e were carried out by combining a small excess (1.5 equiv per polymer repeat unit) of each derivative with **P1** in tetrahydrofuran at room temperature (Scheme 3). Upon mixing, effervescence was immediately observed as a result of N<sub>2</sub> evolution, providing visual confirmation that the reaction was occurring. Stirring the reaction mixture at room temperature for 30 minutes resulted in a visible increase in solution viscosity, and quantitative conversion of the tetrazines to the cycloadducts. This could be easily confirmed by the complete disappearance of signals at 7.05 and 7.90 ppm in the NMR spectrum, which correspond to the furyl protons that are adjacent to the tetrazine groups in P1 (Figure 1a). It should be noted that, because the TCO derivatives are not symmetrical about the  $C_2$  axis, each of the dihydropyridazine subunits within the products (P2, P2a-f) is formed as a mixture of two regioisomers (Scheme 3b), which considerably complicates the <sup>1</sup>H-NMR spectra associated with these products. It should also be noted that IEDDA of transcyclooctenes onto s-tetrazines yields 4,5-dihydropyridazines, which readily tautomerize into 1,4-dihydropyridazines as evident by the presence of an N-H resonance between 8 and 9 ppm in the <sup>1</sup>H-NMR spectra (see spectrum for P2a in Figure 1 a, as well as additional <sup>1</sup>H-NMR spectra in the Supporting Information, Figures S27–S33). In addition to NMR analysis, IR corroborated the introduction of the TCO derivatives on the polymer backbone with the strong carbonyl stretch of the primary carbamates observed at 1708-1722 cm<sup>-1</sup> for each of the products (see Supporting Information, Figures S72-S78). The molecular weight of each of the functionalized product polymers was measured by both GPC and NMR, with observed values provided in Table 1. In most cases, the apparent number average molecular weight  $(M_n)$ observed by GPC was in good agreement with the corresponding value from NMR, both of which indicated a small



**Scheme 3.** Inverse Electron Demand Diels Alder (IEDDA) reaction to functionalize polymer **P1** with TCO derivatives (a). Illustration of the two regioisomers that are possible at each clicked repeat unit (b).



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*Figure 1.* a) NMR data illustrating the sequential transformation of **P1** upon clicking and oxidation. b) UV/Vis absorption data for **P1** (black), **P2-a** (blue), and **P3-a** (green), illustrating the effect of breaking conjugation (hypsochromic shift) upon click coupling, followed by reformation of conjugated structures upon oxidation (bathochromic shift).

Table 1: GPC and NMR molecular weights for polymers produced.

Polymer	NMR Mn [kDa]	DP	GPC Mn [kDa]	Mw [kDa]	Ð
P1	36.3	44	38.8	63.7	1.64
P2	36.0	39	12.2	15.0	1.23
P2 a	53.3	45	46.8	67.8	1.45
P2b	45.9	44	40.9	71.8	1.76
P2 c	45.0	45	39.3	82.5	2.10
P2 d	46.5	44	38.4	79.6	2.07
P2 e	47.2	44	33.5	53.4	1.60
P3	36.8	40	12.9	22.6	1.76
P3 a	51.0	43	24.6	45.4	1.84
Р3 Ь	47.5	45	14.1	24.2	1.72
P3 c	41.8	42	16.4	28.8	1.76
P3 d	45.9	44	25.5	45.4	2.08
P3 e	56.6	44	17.8	33.1	1.86

increase in molecular weight as a result of the side chains that were appended via the IEDDA reactions. In the case of **P2**, the significant decrease in apparent molecular weight from the GPC measurement was likely caused by interactions between the hydroxyl groups in this product with the stationary phase of the GPC columns, which delays its elution and results in an observed  $M_n$  value that is lower than the actual value. Additionally, reaction progress could be moni-

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tored by UV/Vis spectroscopy, where the strong absorption of **P1**, centered around 460 nm, undergoes a significant hypsochromic shift to 400 nm in **P2**. The extent of this shift for each of the polymers, including **P2a–e**, is given in Table 2, and correlates well with steric hindrance from the appended sidechain, which would result in a twisting of the polymer backbone and decreased conjugation length. In addition, while the unreacted poly(tetrazine) **P1** exhibited only very weak fluorescence, the cycloadduct dihydropyridazine polymers (**P2**, **P2a–e**) exhibited much stronger fluorescence, with a broad emission band centered around 510 nm (Supporting Information, Figures S54–S59). In fact, the onset of fluorescence could be observed by carrying out the reaction while irradiating the reaction vessel with UV light at 365 nm (video 1, Supporting Information).

**Table 2:** Absorption spectrum  $\lambda_{max}$  values and resultant hypsochromic and bathochromic shifts produced upon cycloaddition and oxidation of the polymers, respectively.

Polymer	λ <sub>max</sub> [nm]	Polymer	λ <sub>max</sub> [nm]	Shift [nm]	Polymer	λ <sub>max</sub> [nm]	Shift [nm]
P1	457	P2 P2 a P2 b P2 c P2 d P2 e	400 388 402 412 404 405	-57 -69 -55 -45 -53 -52	P3 P3 a P3 b P3 c P3 d P3 e	423 426 424 428 428 428 427	+23 +38 +22 +16 +24 +22

#### Reaction Kinetics of P1 with TCO-OH (5)

To determine the rate of the reaction between the poly(tetrazine) P1 and TCO-OH (5), a kinetics study was performed. The reaction was carried out in a quartz cuvette with equimolar concentrations of both P1 and 5 (0.242 mM), and reaction progress was monitored by measuring the absorption of the reaction mixture at 500 nm over the course of 90 min. The starting polymer, P1, exhibits a strong absorption at this wavelength, while the product, P2, exhibits negligible absorption (Figure 1b). The kinetics study was performed in triplicate, and resulted in an average second order rate constant of  $1.25 \pm 0.07 \text{ M}^{-1}\text{s}^{-1}$  (see Supporting Information). Although a modest rate constant for typical tetrazine ligations with trans-cyclooctenes, the IEDDA on P1 is two orders of magnitude faster than strain-promoted alkyne-azide cylooaddition (SPAAC) reactions that we have previously carried out on polymeric substrates.<sup>[32]</sup>

#### Oxidation of Poly(1,4-Dihydropyridazines)

Considering the goal of producing a set of homologous conjugated polymers, it was necessary to oxidize the dihydropyridazine rings in **P2**, and **P2a–e** in order to aromatize them into pyridazines. This was accomplished by treating each of the polymers with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in THF at room temperature for 1 h, resulting in polymers **P3**, **P3a–e** (Scheme 4). Upon oxidation, <sup>1</sup>H-NMR showed a clean disappearance of the N-H resonance corresponding to the dihydropyridazine between 8 and 9 ppm (Figure 1 a), indicating that the oxidation was effective. The IR spectra of the product polymers did not change appreciably upon oxidation (Figures S72–S79), but the absorption spectrum of each polymer underwent a bathochromic shift, ranging from 16 to 38 nm (Table 2 and Figures S47–S52). This indicates that the formation of pyridazine rings results in increased conjugation along the polymer slightly increased in intensity, and spectra exhibited small changes to fine structure (see Supporting Information, Figures S54–S59). The changes in absorption and emission spectra for **P3** relative to the original polymer **P1** are illustrated in Figure 2, which



*Figure 2.* Overlay of absorption and emission spectra comparing P1 and P3.

shows the significant hypsochromic shift in the absorption spectrum, and the increase in fluorescence intensity. Interestingly, upon oxidation of the dihydropyridazine backbone to yield the poly(pyridazines) P3, P3a-e, the observed GPC molecular weights decrease, while the NMR molecular weights remain relatively unchanged. The largest decrease was for P3, which can again be explained by the presence of hydroxyl groups along the polymer backbone that interact with the stationary phase of the column. The lower than expected GPC values for P3a-e indicate that these structures must either adopt a more compact conformation in solution than the P2 series, or that the formation of the pyridazine rings also results in enhanced interaction with the stationary phase, causing delayed elution. Chain scission as a result of the oxidation process was ruled out by <sup>1</sup>H-NMR end-group analysis (see Figures S34-S39), which indicated that the molecular weights were not significantly changed upon oxidation (Table 1). TGA analysis of the product polymers was also carried out under Ar atmosphere to determine their



Scheme 4. Oxidation of the clicked poly(1,4-dihydropyridazine) series.

Angew. Chem. Int. Ed. 2020, 59, 2-9

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thermal decomposition patterns and temperatures (see Supporting Information, Figures S63–S68). In all cases, two distinct decompositions were observed, which correspond to the loss of the Diels–Alder adducts at 200–300 °C (4–23 % mass loss, depending on the molecular weight of the TCO derivative), followed by the loss of the hexadecyl side-chains of the fluorenyl units at  $\approx 400$  °C (50–61 % mass loss).

#### Analysis of Polymer Geometry—DFT Calculations

In order to probe the effect of backbone functionalization via IEDDA on the overall structure of the polymer, we carried out modeling studies using semi-empirical methods (Parametric Method 3, PM3). This involved construction of three separate oligomers (3 repeat units each) corresponding to the structures prior to functionalization, post functionalization with 5, and after oxidation of the dihydropyridazines with DDQ, followed by geometry optimization of each structure. As shown in Figure 3, the geometry of starting polymer P1 is planar, as would be expected from its conjugated structure. Upon IEDDA with 5, the geometry retains much of its planarity, with only slight perturbations caused by the introduction of cyclooctyl rings and the decreased conjugation that results from formation of the dihydropyridazines. After oxidation, the calculations indicate that the P3 polymer backbone adopts a slightly puckered structure relative to the planarity of P1, but overall remains relatively planar. This puckering in P2 and P3 is likely caused by steric interactions between the cyclooctyl ring and the neighbouring furans, which changes the angle between the two ring structures away from planarity. To corroborate this, we carried out additional DFT geometry optimizations on truncated model compounds and found that the coplanar rings on either side of the tetrazine unit adopt a  $\approx 30^{\circ}$  angle in the puckered dihydropyridazine structure, but only a 4° angle upon oxidation to the more planar pyridazine (Figure S3). These slight changes between P1, P2, and P3 might also explain some of the differences in apparent hydrodynamic diameter that contribute to the changes in molecular weight values observed from GPC.



Figure 3. Optimized geometry (PM3) of trimers P1 (a), P2 (b), and P3 (c). Note the minimal amount of puckering in the backbones of P2 and P3 upon undergoing IEDDA. Alkyl chains were replaced with methyl groups to ease computational loads.

## Post-Polymerization IEDDA of 5 kDa PEG Onto P1

To further test the efficiency of the IEDDA cycloaddition reaction in functionalizing the polymer backbone, a 5 kDa poly(ethylene glycol)-TCO derivative 7 f was grafted onto P1. Reaction with 7f was found to be significantly slower than with the small molecule derivatives, requiring slight heating and a longer reaction time. Thus, a small excess (1.2 equiv.) of 7 f was stirred with P1 at 40 °C for 8 hours, which resulted in quantitative functionalization of the backbone. Dialysis in water over 72 h using a 50 kDa molecular weight cutoff dialysis membrane allowed for the removal of the excess PEG-TCO carbamate from the reaction mixture, leaving behind the pure dihydropyridazine graft copolymer P2 f. Figure 4 shows the <sup>1</sup>H-NMR spectrum of **P2 f** overlaid with the starting polymer P1. The aromatic region displays a similar shifting of the furyl proton resonances as observed in the small molecule cycloadditions. Additionally, a large resonance corresponding to the methylene protons of the PEG chains is observed at 3.7 ppm, indicating the presence of the graft on the P1 backbone. Consistent with the small molecule click reactions, an hypsochromic shift is observed in the polymer UV/Vis spectrum, though the shift is much larger in the case of **P2 f**, amounting to over 110 nm (Figure S53). This large blue-shift is likely caused by a significant twisting of the polymer backbone away from conjugation in order to accommodate all of the appended PEG chains. The molecular weight of PEG graft poly(1,4-dihydropyridazine) P2f could not be accurately measured by GPC due to interactions between the PEG grafts and the column stationary phase, leading to extensive retention on the column. Additionally, the functional methoxy end-group handle could not be accurately integrated via <sup>1</sup>H-NMR due to overlap of the signals with those of the PEG methylene units. As a result, only a theoretical molecular weight is listed in the Supporting



*Figure 4.* (a) <sup>1</sup>H-NMR spectra of **P1** and **P2 f**, illustrating the shift of furyl aromatic signals and the appearance of PEG signals upon click coupling. b) Photograph of the biphasic mixtures of water and toluene where **P1** remains in the organic phase (i), while **P2 f** dissolves in the aqueous phase (ii). c) Photograph of the same two mixtures under UV light irradiation (365 nm), showing that **P1** is not appreciably fluorescent, while **P2 f** exhibits strong emission.

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Information. Thermogravimetric analysis of **P2 f** showed a single, large mass loss at approximately 400 °C, which corresponds to the decomposition of the grafted PEG chains that make up nearly 90% of the mass of **P2 f**.

The PEG-grafted **P2 f** was found to exhibit a significant solubility change relative to the parent polymer, **P1**. While **P1** is soluble in organic solvents, such as chloroform, dichloromethane, tetrahydrofuran, and toluene, **P2 f** exhibits solubility in more polar organics (tetrahydrofuran, alcohols) and was even soluble in water. Figure 4b illustrates this difference, showing that **P1** remains in the organic phase of a biphasic mixture of toluene and water, while **P2 f** prefers the aqueous phase. When irradiated with a hand-held UV lamp at 365 nm, only the graft copolymer exhibits fluorescence, with a  $\lambda_{em}$  at  $\approx 475$  nm (Figure 4c; see Supporting Information, Figure S60, for the complete emission spectrum).

### Crosslinking of P1 with Bis-TCO Carbamate Derivative (8)

In addition to the grafting of poly(ethylene glycol) onto the backbone of **P1**, it is also possible to carry out a crosslinking reaction. Reaction of the nitrophenyl carbonate **6** with 1,4-diaminobutane resulted in the difunctional crosslinker **8** (Figure 5), which could be subsequently used to carry out IEDDA chemistry to crosslink polymer **P1**. The crosslinking chemistry occurs rapidly over the course of several minutes, liberating a crosslinked network polymer (see Supporting Information, Video 2, for a video of the process). The N<sub>2</sub> gas evolved from this reaction acts as a blowing agent, resulting in



*Figure 5.* a) Use of the bis-TCO crosslinker **8** to crosslink **P1** and produce the network polymer **P4**. b) Photograph of the crosslinked foam.

an intractable red foam as the product. The foam was treated with DDQ to oxidize any dihydropyridazines and isolate the crosslinked **P4** (Figure 5). The spongy red solid was found to exhibit fluorescence when irradiated with a hand-held UV lamp at 365 nm.

### Conclusion

We have demonstrated the synthesis of a high molecular weight conjugated polymer containing reactive s-tetrazine moieties within the backbone. Functionalization of the progenitor poly(tetrazine) P1 was conducted via IEDDA using a series of TCO derivatives to generate a small library of dihydropyridazine polymers (P2, P2a-e) which were further oxidized to produce the corresponding conjugated poly(pyridazines) (P3, P3a-e). The product polymers, both before and after oxidation, exhibited substantial hypsochromic shifts in absorption, and increased emission intensity, relative to P1. Molecular modeling studies showed that, upon undergoing the "click" reaction, the pyridazine rings along the polymer backbone do not exhibit a significant change in conformation, remaining relatively planar. NMR analysis indicated that the "click" reaction did not alter the average degree of polymerization of the polymers. Additionally, IEDDA "click" reactions on the backbone of P1 occur at rates comparable to those of small molecule s-tetrazines with TCO. The high efficiency of the IEDDA reaction was demonstrated by grafting a 5 kDa poly(ethylene glycol)-TCO chain, a reaction that resulted in quantitative functionalization over 8 hours at 40 °C. Finally, the P1 backbone can be rapidly crosslinked with a difunctional TCO resulting in the generation of a foamlike material.

### Acknowledgements

Financial support for this work was provided by the Natural Science and Engineering Research Council of Canada (NSERC). V.K. is grateful for support through the NSERC-PGS-D program. We further thank Dr. S. A. McNelles for assistance with dialysis and acquisition of MALDI spectra.

# **Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** click coupling · conjugated polymers · functionalization · inverse-electron-demand Diels– Alder reaction · tetrazine

 Polymers for Light-Emitting Devices and Displays, (Eds.: Inamuddin, R. Boddula, M. I. Ahamed, A. M. Asiri), Wiley-Scrivener, Hoboken, 2020.

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Manuscript received: August 6, 2020

Revised manuscript received: October 17, 2020

Version of record online:

www.angewandte.org
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# **Research Articles**



# **Research Articles**

# Conjugated Polymers

V. Kardelis, M. M. Denk,

A. Adronov\* \_\_\_\_

Click-Functionalization of

a Poly(Tetrazine)-co-Fluorene-Conjugated Polymer with a Series of *trans*-Cyclooctene Derivatives



A conjugated polymer containing tetrazine groups in the backbone was prepared and found to undergo rapid inverse-electron-demand Diels–Alder (IEDDA) click chemistry, enabling facile functionalization with a variety of *trans*cyclooctene derivatives. The product polymers change color, become fluorescent, and exhibit changes to their physical properties, such as solubility, depending on the functionality that is appended.