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Mechanism of Janus Polymerization: A DFT Study

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Electronic Supplementary Information

Abstract Janus polymerization is featured as a combination of cationic and anionic growing ends in one living polymer chain. In the copolymerization of THF and CL catalyzed by lutetium triflates and initiated by propylene oxide, three stages are identified by kinetic study including (1) fast cationic polymerization with slow anionic one, (2) fast anionic polymerization with dormant cationic one, and (3) reactivation of cationic polymerization with coupling of anionic and cationic chain ends. In this work, density functional theory (DFT) calculation is employed to investigate the reaction details of ionic polymerization and dormancy. A “tripedal crow” configuration is proposed to illustrate the unique high-coordinated ligand exchange configuration in anionic polymerization in different stages. The trigger of dormancy is determined as chain structures rather than concentration of triflate anion according to both calculation and experimental results.

Keywords Rare earth metal catalysts; Ring-opening polymerization; Ionic polymerization; Reaction mechanism; Quantum chemical computation

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INTRODUCTION

Combining the cationic and anionic polymerizations in one living chain has been realized *via* Janus polymerization as introduced by our group.^[1] Janus polymerization has become an attractive and practical one-pot method for preparing various topological polymers including multi-block copolymers,^[1–3] branched polymers,^[4] mikto-arm star-like polymers,^[5] and polymer brushes.^[6] In 2014, our group firstly reported that tetrahydrofuran (THF) and ϵ -caprolactone (ϵ -CL) were catalyzed by lutetium triflates ($\text{Lu}(\text{OTf})_3$) in the presence of propylene oxide (PO) as initiator, which produced multi-block copolymer with M_w up to 300 kg/mol.^[1] Due to the physical cross-linking induced by crystallization of PCL blocks, the biodegradable polymer was both thermoplastic elastomer as thermal-molded film in bulk^[2] and plastics nano-fibers after electrospinning.^[3] Branched poly(tetrahydrofuran), mikto-arm star-like polyester-polyether materials, and heterografted molecular polymer brushes^[6] exhibited unique self-healing and self-assembly properties.^[4,5] Very recently, we published the second example of the Janus polymerization of CL with 3,3-bis(chloromethyl) oxacyclobutane.^[7]

Janus polymerization proceeds in three stages as demon-

strated by kinetic investigation (Fig. S1 in electronic supplementary information, ESI).^[1] Active cationic and anionic centres are simultaneously generated in Stage I. In Stage II, cationic chain end turns into dormant cation species, and fast anionic polymerization is found in anionic end. When ϵ -CL reaches high conversion above 90%, cationic chain end resumes active and intermolecular coupling reactions happen between anionic and cationic chain ends in Stage III. It is essential to figure out the chemical natures of cationic and anionic centres in the three stages, as well as corresponding elementary reactions of polymerization including initiation and propagation.

In this contribution, we use density functional theory (DFT) calculations to reveal the mechanism of Janus polymerization. The molecular structures of active species in Stages I and II are detailedly investigated, as well as the corresponding propagation process. Three steps, *i.e.* carbonyl addition, ligand exchange, and ring-opening, in propagation on anionic end are confirmed, and special high-coordinated transition state is firstly reported in ligand exchange of rare earth triflate catalysis.

CALCULATION DETAILS

Density functional theory (DFT) calculations were employed to optimize all geometries of intermediates under tight criteria using B3LYP^[8,9]/6-31g(d,p) methods. Single-point energy calculation results in 3OTf-route were obtained under B3LYP/aug-cc-pVTZ//B3LYP/6-31G(d,p) level. Frequency calculations were carried out to ensure that the intermediates

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and transition states (TSs) had zero and one imaginary frequency, respectively. All reaction pathways of TSs were checked by intrinsic reaction coordinate (IRC).^[10] Thermal correction to Gibbs free energies was obtained at 298.2 K and 1.013×10^5 Pa. All calculations were carried out using Gaussian 16 program as we reported before.^[11–13] Some pictures were rendered with CYL-View.^[14] In this work, $\text{Sc}(\text{OTf})_3$ was used to represent rare earth triflates ($\text{RE}(\text{OTf})_3$) catalyst as a model catalyst. Ethylene oxide (EO) was chosen as a model initiator among all possible epoxy initiators.

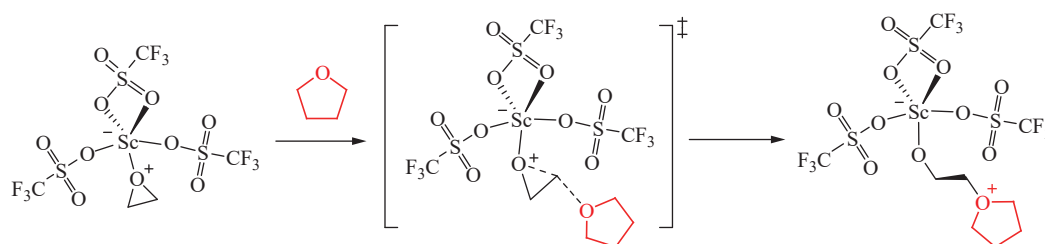
RESULTS AND DISCUSSION

According to DFT calculations, the scandium atom in $\text{Sc}(\text{OTf})_3/\text{EO}$ is penta-coordinated in a distorted trigonal bipyramid configuration as shown in Fig. S2 (in ESI). The three triflate ligands are in two nonequivalent hybridization,

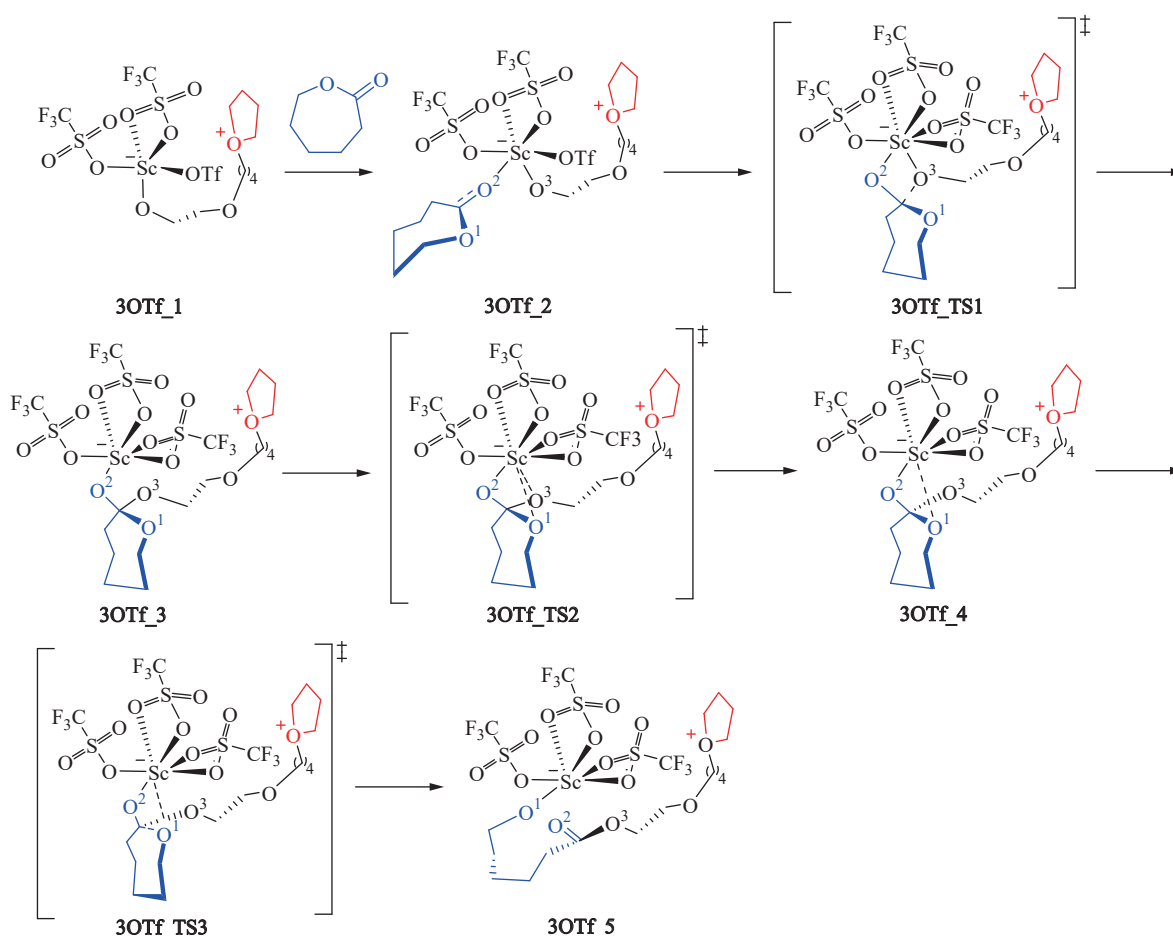
including an η^2 -bond with a $\text{Sc}-\text{O}$ distance of 2.15 (2.17) Å and two η^1 -bond with 1.95 (1.96) Å. The $\text{Sc}-\text{O}(\text{EO})$ distance (2.11 Å) is in between of η^1 - and η^2 - $\text{Sc}-\text{O}(\text{OTf})$, and the oxygen atom of EO has less negative charge (−0.529) than those of triflates (−0.635 to −0.712).

The initiation process in Janus polymerization is recognized as the formation of two separated active ion centres as shown in Scheme 1. After nucleophilic attack induced by THF *via* a typical $\text{S}_{\text{N}}2$ pathway, active cation and centres are formed, *i.e.* oxonium and $\text{Sc}-\text{O}$, respectively, with a Gibbs free energy barrier of 16.3 kcal/mol. Separated cationic and anionic centres are facilitated with a distance of scandium and oxonium over 4.9 Å.

In Stage I, polymerization of CL is identified with controllable and living manner, which takes part in both propagation sites. In anionic $\text{Sc}-\text{O}$ side, CL propagations appear in a successive process consisting of coordination, carbonyl ad-



Scheme 1 Initiation process of Janus polymerization



Scheme 2 Propagation process of CL on anionic side in Stage I of Janus polymerization

dition, ligand exchange, and ring cleavage, which leaves similar active anionic centre as summarized in Scheme 2. It consists with the mechanism of CL ROP initiated by rare earth alkoxide reported before.^[15,16] After coordinating with Sc, CL rotates along Sc–O² bond so that carbonyl group gets closer to Sc–O³ bond. The Sc–O³ distance increases from 1.84 Å (**3OTf_2**) to 2.25 Å (**3OTf_3**) via a four-member ring planar TS of carbonyl addition (**3OTf_TS1**). It is worthy of noticing that the propagation does not unimpededly reach ring opening due to the bulk steric hindrance constituted by multiple ligands, which blocks the immediate exchange of Sc–O³ to O¹. Herein we revealed a octa-coordinated TS ([Sc](η^3 -CL)(η^2 -OTf)₂(η^1 -OTf)), **3OTf_TS2** with the highest energy barrier observed during this ligand exchange process. The geometry of **3OTf_TS2** looks like a tripedal crow (a legendary bird representing Sun in Asian mythologies) containing two wings (two (η^2 -OTf) ligands), three claws (η^3 -CL) and a tail (η^1 -OTf) ligand (Fig. 1). Pyramid geometry of Sc–O¹–C–O³ is facilitated when Sc–O³ bond ultimately breaks up (3.74 Å in **3OTf_4**) via Sc migration. After ring-opening process with the TS of **3OTf_TS3**, Sc–O¹ bond is eventually formed as new active anionic centre.

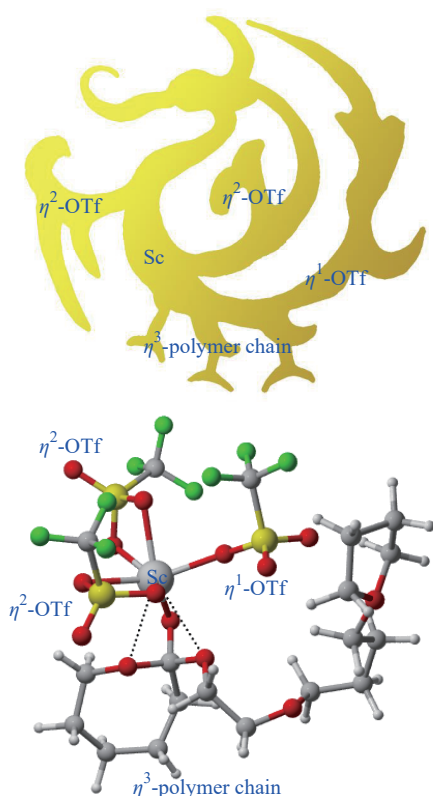


Fig. 1 Geometry of unique octa-coordinated ligand exchange transition state (**3OTf_TS2**) according to DFT calculations under B3LYP/6-31g(d,p). The coordination nature is represented by a tripedal crow featured two wings, three claws, and a tail, which mean two η^2 -bonded OTf ligands, three η^2 -bonded oxygen atoms, and one η^1 -bonded OTf ligand.

The rate-determining step of CL ROP at the RO-Sc(OTf)₃ end is considered as the ligand exchange with ΔG of 38.7 kcal/mol (blue line in Fig. 2). The rate-determining step and

reaction route remain the same under B3LYP/aug-cc-pVTZ//B3LYP/6-31G(d,p) level as shown in Fig. S3 (in ESI).

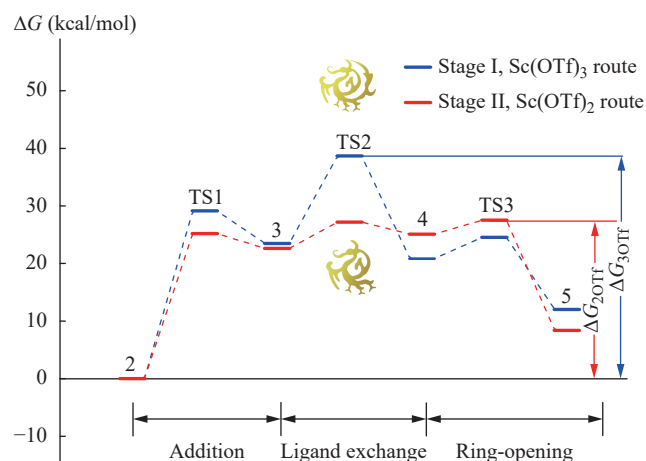


Fig. 2 Energy profiles of anionic polymerization in Stage I (blue) and Stage II (red) according to DFT calculations under B3LYP/6-31g(d,p). ΔG of rate determining step: $\Delta G_{3OTf} = 38.7$ kcal/mol, $\Delta G_{2OTf} = 27.5$ kcal/mol. Two tripedal crows are used to represent structures of **3OTf_TS2** and **2OTf_TS2**. In Stage II, ligand exchange transition state changes from octa-coordinated to septa-coordinated one, which featured an anurous bird (two wings, three claws but without a tail) as shown in the figure. The difference of Gibbs energy barrier of rate determining step: $\Delta\Delta G_{rate} = \Delta G_{3OTf} - \Delta G_{2OTf} = 11.2$ kcal/mol.

In Stage I, copolymerization in cationic centre proceeds in a living manner, which takes the entire rare earth compound as counter ion in a cyclic configuration. A S_N2 mechanism is favoured in cationic propagation on THF or CL oxonium as shown in Scheme S1 (in ESI) with the corresponding Gibbs free energy barriers suggesting a THF-preferred random copolymerization, which agrees well with the experimental results that the reactivity ratios of THF and CL are 2.03 and 1.23, respectively.^[5]

The dormancy of cationic end, which is attributed to ring-opening of oxonium via OTf ligand leaving from anionic end, is recognized as the beginning of Stage II. The intramolecular migration of OTf ligand in the ring configuration of propagating chains is the trigger of the dormancy since experimental results confirmed that excess OTf anion showed no obvious influence on total polymerization process (Table 1). The dormancy is confirmed to take place between 48 and 144 h (Table 1, runs 1–3) and additive Na-OTf is considered as no effect before dormancy (runs 2 and 4–6 in Table 1) with comparable polydispersities ($\bar{D}$) and number-average molecular weights (M_n), as well as those in Stage II (runs 3, 7, and 8 in Table 1).

Reversible ring-opening on oxonium via nucleophilic attack of OTf (Fig. 3) is the reason for the dormancy of cationic ROP. Stable covalent bond species are observed in both THF oxonium and CL oxonium routes. The dormancy of THF oxonium is preferred due to lower energy barrier ($\Delta\Delta G_1 = 5.6$ kcal/mol) and more stable covalent species ($\Delta\Delta G_2 = 7.6$ kcal/mol, Fig. 3) than CL end.

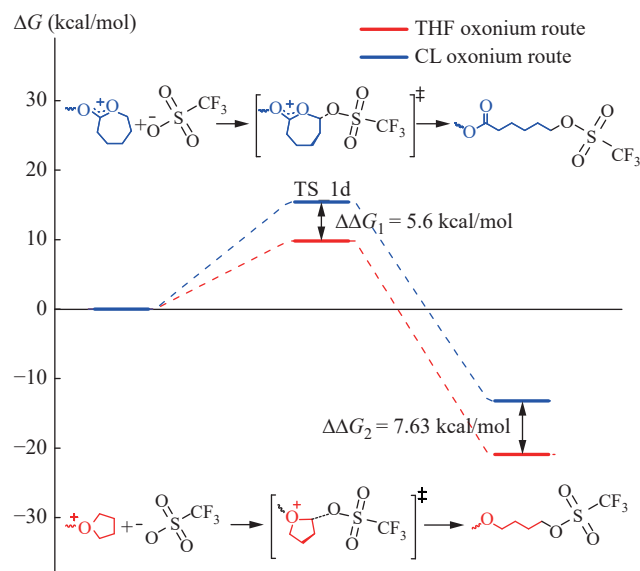
Accompanying with the leaving of OTf ligand, anionic polymerization accelerates as benefiting from the enhanced

Table 1 Janus polymerization of THF and CL catalyzed by Lu(OTf)₃/PO at 25 °C with and without the addition of NaOTf

Run	Lu(OTf) ₃ :PO:CL: THF:NaOTf (molar ratio)	Time (h)	Conv. ^a (%)		<i>D</i> ^b	<i>M</i> _{n,SEC} ^b (kDa)	<i>M</i> _{n,theo} ^c (kDa)
			THF	CL			
1	1:1.5:200:200:0	20	1.3	29.6	1.13	5.83	6.98
2		48	3.0	38.0	1.26	13.18	9.17
3		144	5.8	86.5	1.35	13.02	20.65
4	1:1.5:200:200:0.1	48	3.0	37.2	1.20	13.44	8.97
5	1:1.5:200:200:0.3	48	3.2	36.8	1.20	12.74	8.91
6	1:1.5:200:200:0.6	48	3.0	39.4	1.19	13.99	9.49
7	1:1.5:200:200:5	144	6.2	>99	1.42	15.81	23.78
8	1:1.5:200:200:10	144	7.5	>99	1.41	16.31	23.97

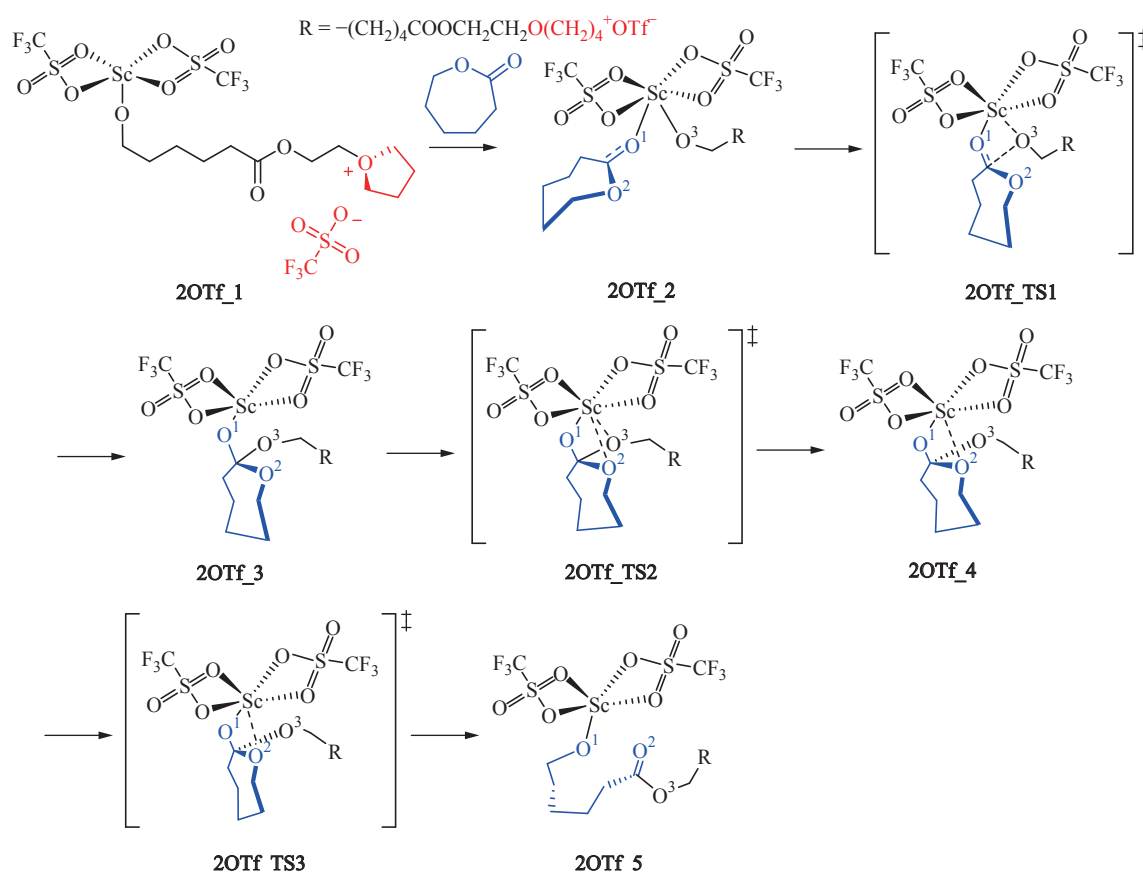
^a Conversions were determined by ¹H-NMR; ^b *M*_n and *D* were determined by SEC; ^c Calculated according to *M*_{n,theo} = 200 × Conv.(CL) × 114.142 + 200 × Conv.(THF) × 72.11 + 58

electrophilicity of Sc center as well as lower steric hindrance around Sc—O bond. Similar to the propagation in Stage I, coordination, carbonyl addition, ligand exchange, and ring-opening are confirmed by DFT calculations, with preference of η^2 -bonded OTf ligand as shown in Scheme 3. The TS of ligand exchange (2OTf_TS2) is observed as a sept-coordinated geometry [Sc]((η^3 -CL)(η^2 -OTf)₂), like an anurous golden bird (red line in Fig. 2). It is of interest to note that the highest energy barrier is found in ring-opening step instead of the ligand exchange step, with a $\Delta\Delta G_{\text{rate}}$ of 11.2 kcal/mol decrease compared with Sc(OTf)₃ route, which explains the accelerated propagation of CL in Stage II. After ring-opening, active Sc—O bond is formed as a new

**Fig. 3** Energy profile of the dormancy of THF (red) and CL (blue) oxonium based on DFT calculations ($\Delta\Delta G_1 = 5.6$ kcal/mol, $\Delta\Delta G_2 = 7.6$ kcal/mol)

propagation end.

This high energy barrier (27.5 kcal/mol) is in good agreement with a slow reaction rate of Janus polymerization (up to several days),^[1] compared with the homopolymerization of CL initiated by RE(OTf)₃/iPrONa system as reported before.^[17]

**Scheme 3** Propagation process of CL on anionic side in Stage II of Janus polymerization

CONCLUSIONS

In this contribution, we revealed in detail the elementary reactions of initiation, dormancy of cationic end, as well as cationic and anionic propagations in Janus polymerization. With a model compound of the rare earth triflate catalyst, the highly coordinated TS and ligand exchange reaction are investigated firstly *via* DFT calculations, which explains slow polymerization rate in Stage I and acceleration in Stage II. The tripodal model of 8- and 7-coordinated rare earth TSs is proposed to represent the structures of catalytic centers with a convenient phase to count coordination number as “two wings, three claws with/without a tail”. Understanding the mechanism of Janus polymerization lights the way to discover more catalysts and monomers in this complicated system. The coupling reaction between chain-ends in Stage III establishes step-growth polymerization in a diffusion-controlled process, and the investigation is in progress.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-019-2318-9>.

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