

Supporting Information

Polydiacetylene and its Composites Having Longer Effective Conjugation Lengths and Meanwhile Tunable Third-Order Nonlinear Optical Absorption

Gang Wang, Yanran Li, Xiayun Huang*, Daoyong Chen*

State Key Laboratory of Molecular Engineering of Polymers, Department of
Macromolecular Science, Fudan University, Shanghai 200438, China

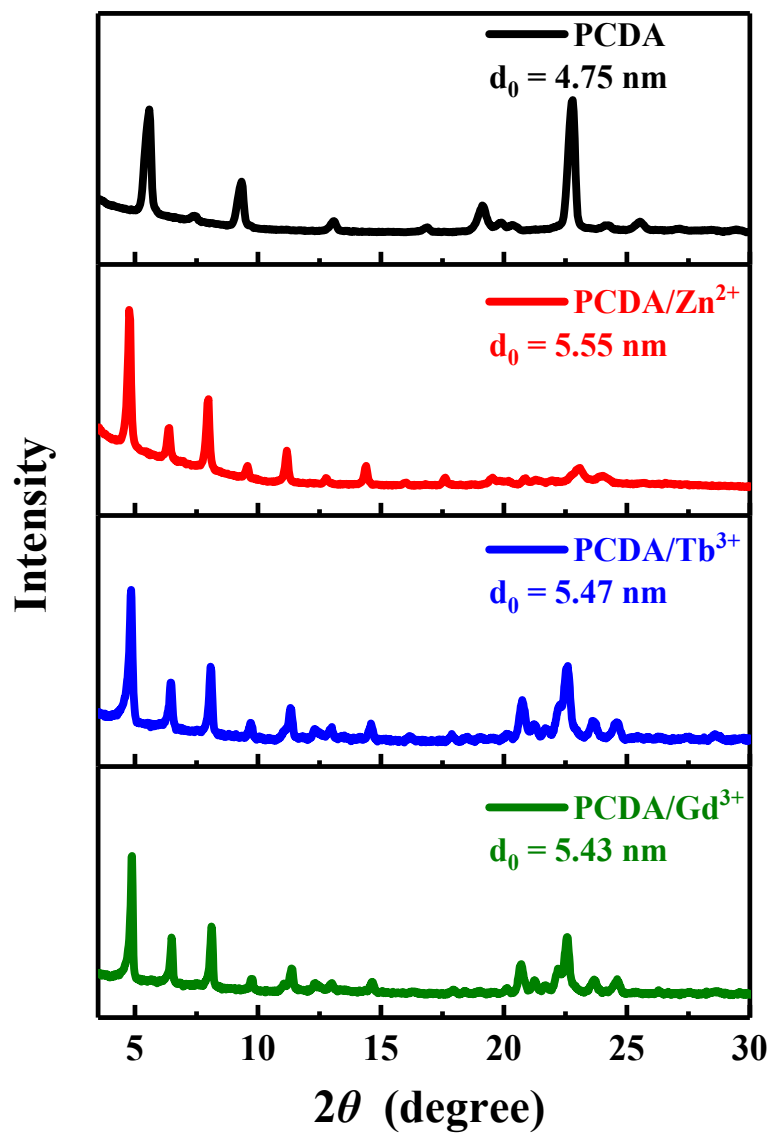


Figure S1. XRD profiles of the PCDA and PCDA/Zn²⁺, PCDA/Tb³⁺, and PCDA/Gd³⁺ annealed for 12 h.

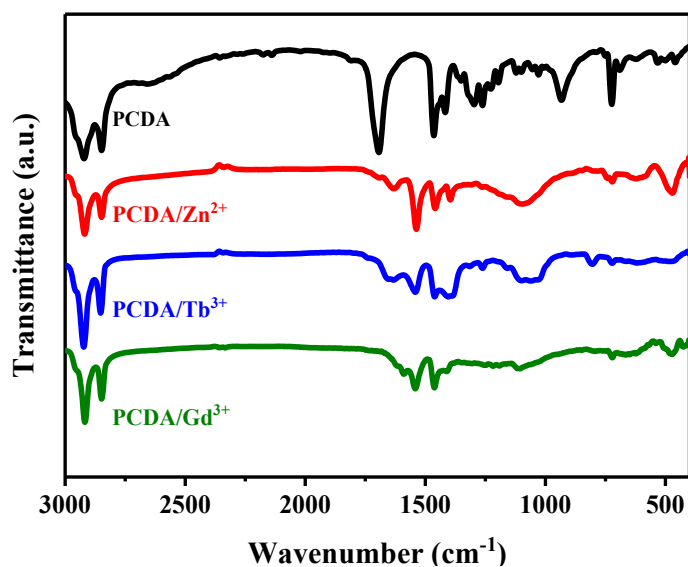


Figure S2. FTIR spectra of the PCDA and PCDA/Zn²⁺, PCDA/Tb³⁺, and PCDA/Gd³⁺ annealed for 12 h. A strong band at 1700 cm⁻¹ is ascribed to the stretching vibration band of the hydrogen bonded carboxyl group. For the PCDA/Mⁿ⁺, the band at 1700 cm⁻¹ disappeared, accompanied with the new bands around 1450 cm⁻¹ and 1540 cm⁻¹ appeared which was ascribed to symmetric ν_s (COO⁻) and asymmetric ν_{as} (COO⁻) stretching vibration of deprotonated carboxyl groups, respectively. According to separation value between ν_s (COO⁻) and ν_{as} (COO⁻) (Table S2), the coordination types were all the chelating bidentate.^{1,2}

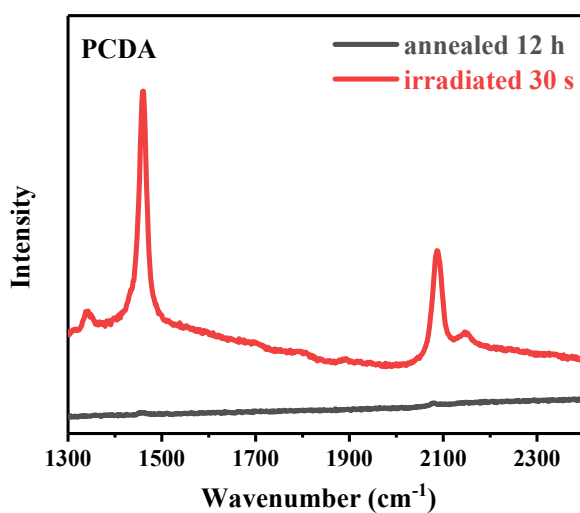


Figure S3. Raman spectra of annealed and irradiated PCDA suspension.

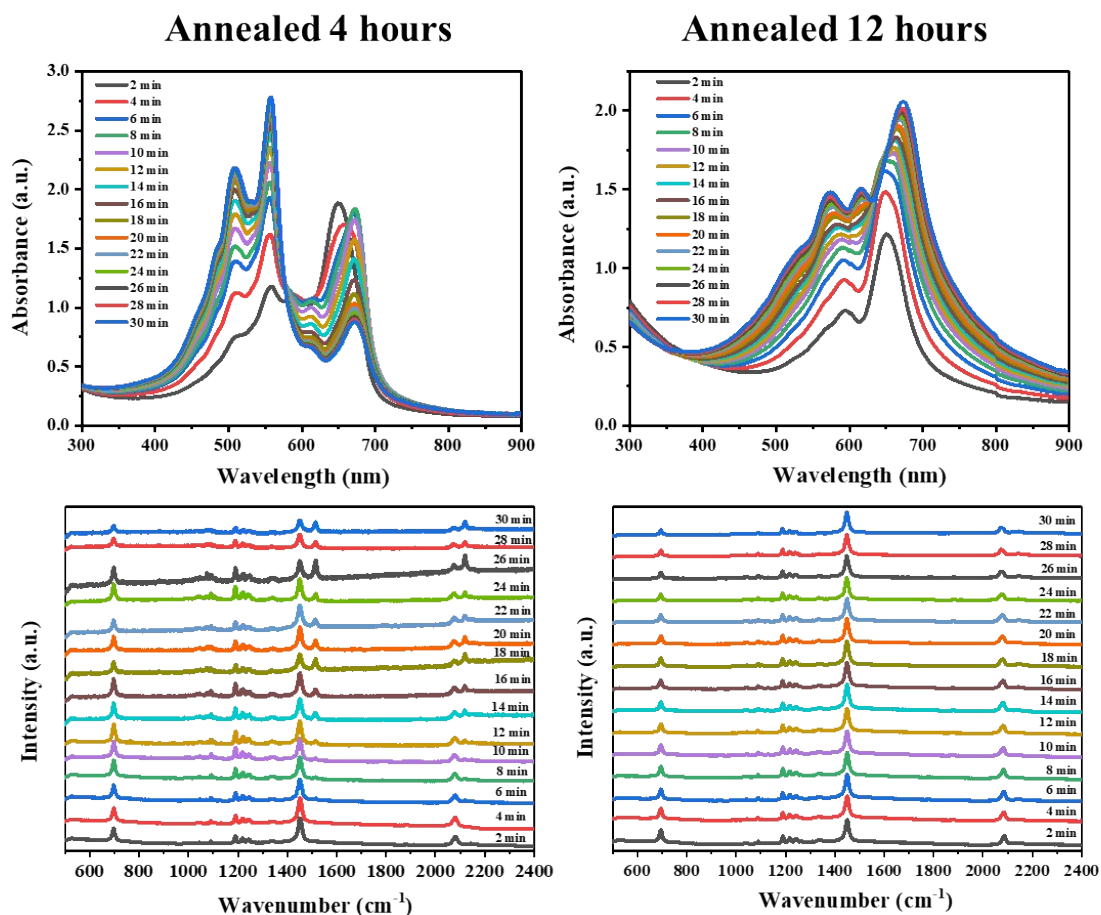


Figure S4. UV-vis absorption spectra (top) and corresponding Raman spectra (bottom) of annealed poly(PCDA) (annealing time was 4 h (left) and 12 h (right)) recorded as a function of irradiation time. For the specimens that have been annealed for 12 h, the maximum absorption did not further bathochromic shift and partial bluish green poly(PCDA) turned into red when the irradiation time is over 30 min.

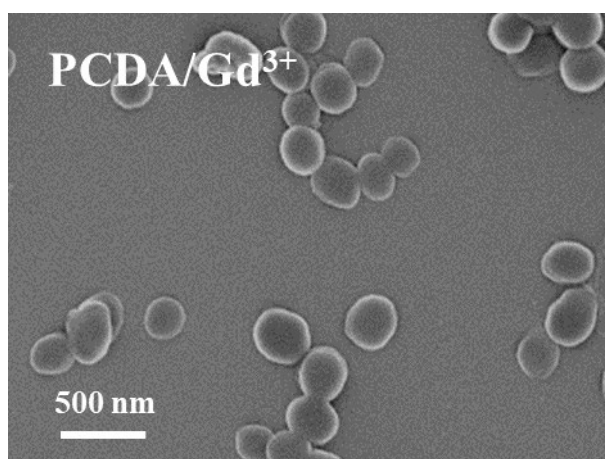


Figure S5. SEM image of PCDA/Gd³⁺.

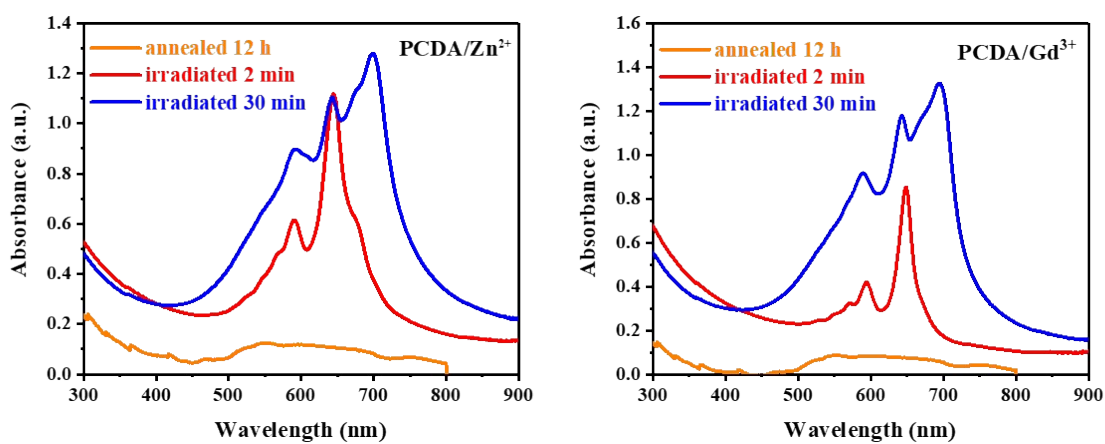


Figure S6. UV-vis absorption spectra of 12 h-annealed PCDA/ metal ions (Zn^{2+} and Gd^{3+}) composite suspensions and the suspensions that expose to the UV irradiation for 2 min and 30 min.

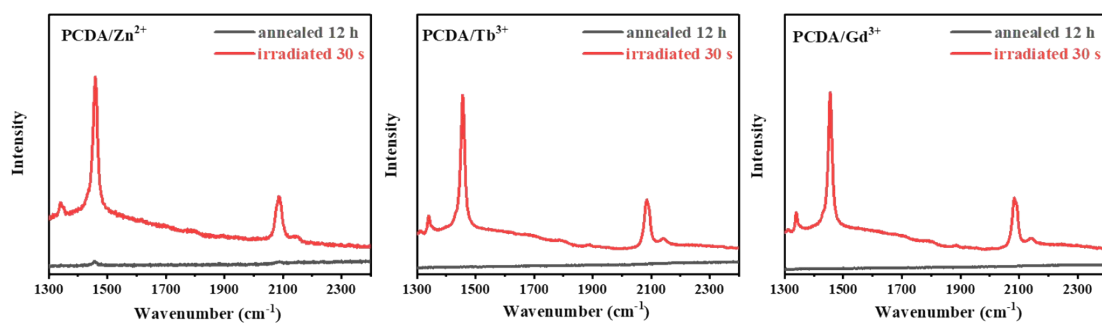


Figure S7. Raman spectra of 12 h-annealed PCDA/ metal ions (Zn^{2+} , Tb^{3+} and Gd^{3+}) composite suspensions and the suspensions that expose to the UV irradiation for 30 s.

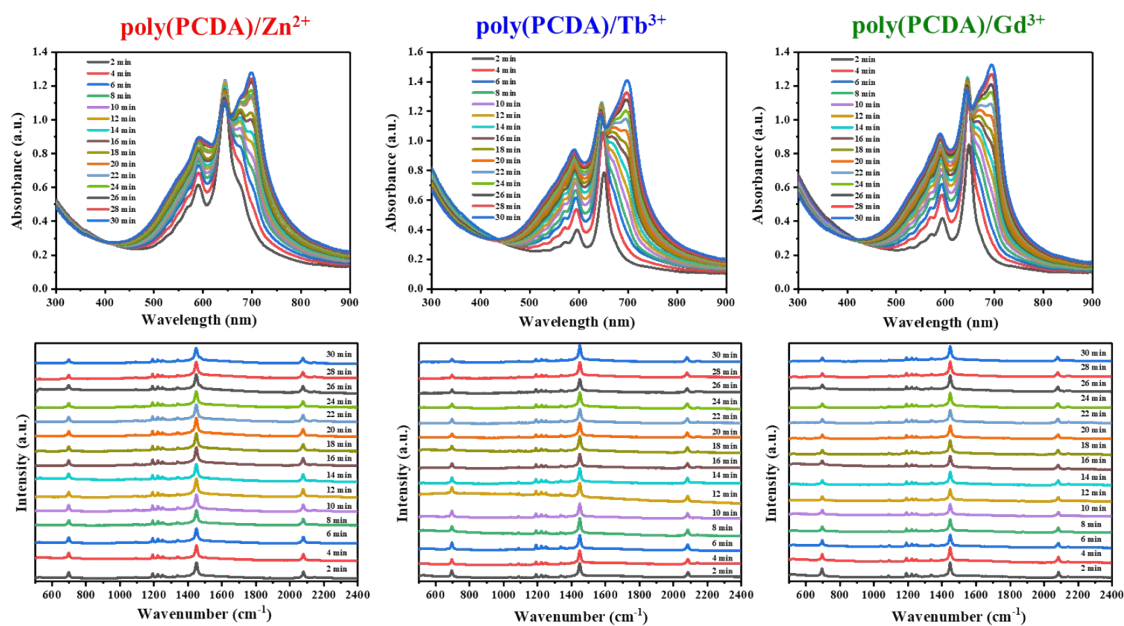


Figure S8. UV-vis absorption (top) and Raman (bottom) spectra of poly(PCDA)/Zn²⁺, poly(PCDA)/Tb³⁺, and poly(PCDA)/Gd³⁺ obtained by irradiating the corresponding PCDA/metal ion composites that have been annealed for 12 h at 254 nm for different time (2-30 min).

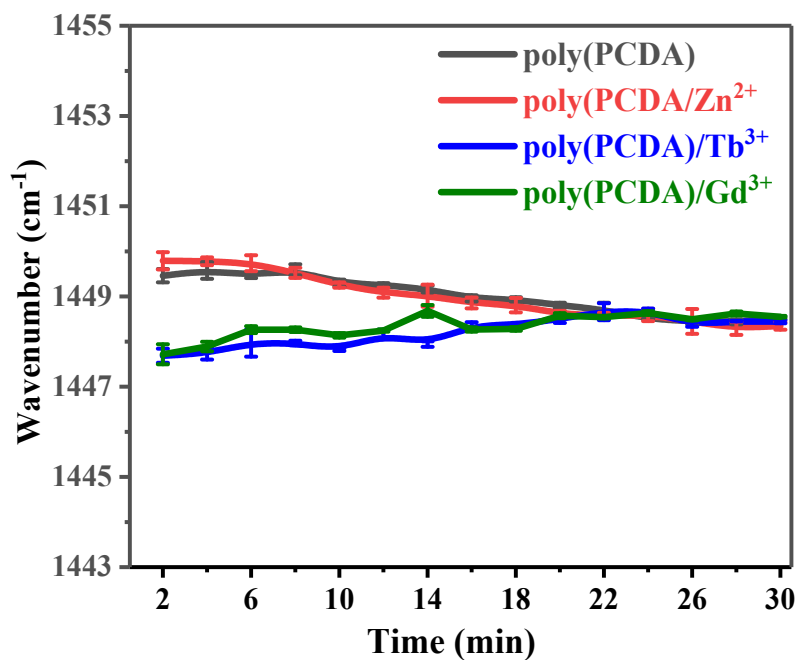


Figure S9. Plot of frequency changes of the double bonds as a function of irradiation time.

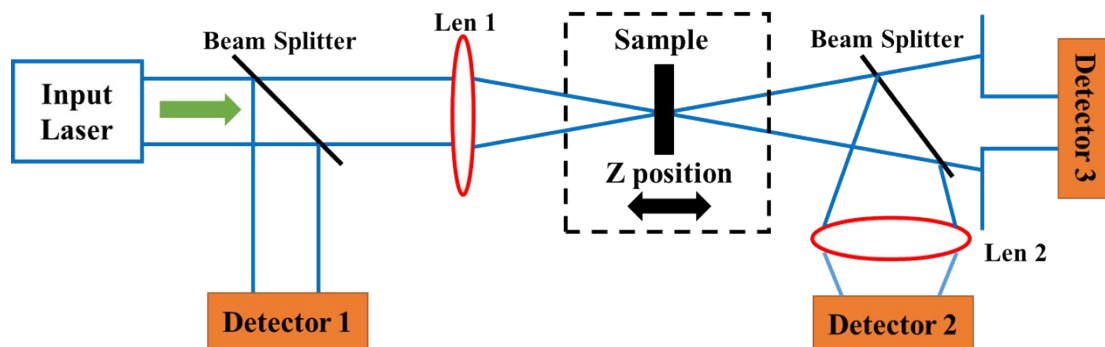


Figure S10. Schematic of the Z-scan measurement with 532 nm laser source.

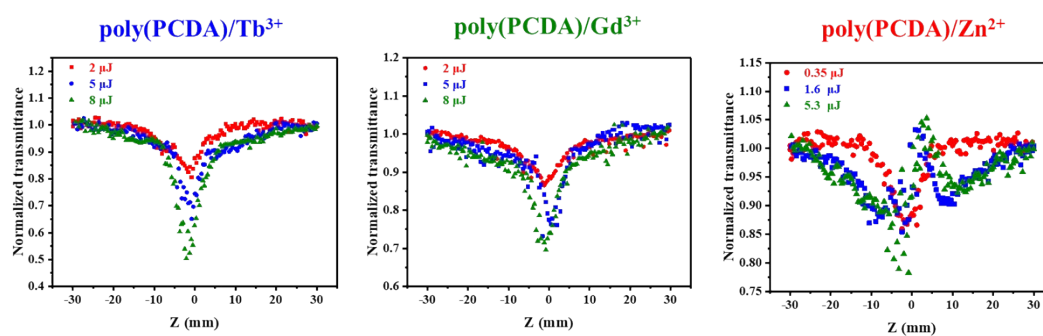


Figure S11. Energy dependent Z-scan curves of poly(PCDA)/Zn²⁺, poly(PCDA)/Tb³⁺, and poly(PCDA)/Gd³⁺.

Table S1. Band assignment of polydiacetylene from the Raman spectra.³

Peak position (cm ⁻¹)	Mode assignment	Peak assignment
1450	C=C stretching	blue PDA
1515	C=C stretching	red PDA
2080	C≡C stretching	blue PDA
2115	C≡C stretching	red PDA

Table S2. Interaction types in the poly(PCDA)/Zn²⁺, poly(PCDA)/Tb³⁺, and poly(PCDA)/Gd³⁺ according to FTIR spectra.

Sample	$\nu_s(\text{COO}^-)$	$\nu_{as}(\text{COO}^-)$	$\Delta(\nu_{as}-\nu_s)$	Interaction type
Poly(PCDA)/Zn ²⁺	1459 cm ⁻¹	1537 cm ⁻¹	78 cm ⁻¹	Chelating bidentate
Poly(PCDA)/Tb ³⁺	1462 cm ⁻¹	1541 cm ⁻¹	79 cm ⁻¹	Chelating bidentate
Poly(PCDA)/Gd ³⁺	1462 cm ⁻¹	1543 cm ⁻¹	81 cm ⁻¹	Chelating bidentate

Table S3. Optical power limiting data of Graphene, C₆₀, and poly(PCDA)/Tb³⁺.

Energy (GW/cm ²)	Optical Limiting (%)		
	Graphene ⁴ T _L = 73%	C ₆₀ ⁴ T _L = 73%	Poly(PCDA)/Tb ³⁺ T _L = 75%
0.048	SA	21	21
0.095	SA	25	25
0.143	SA	29	31
0.190	9	32	32
0.238	34	40	37

SA: Saturated absorption

‡ **Note 1:** According to the simulation by Filhol *et al.*,⁵ the decrease in the C≡C characteristic frequency results from the increase in the conjugation length of polydiacetylene backbone. With increase in the polymerization time, the C≡C characteristic frequencies of both poly(PCDA) and poly(PCDA)/metal ions composites decrease, indicating the increase of the effective conjugation length. The phenomenon that the frequency decrease of C≡C of the composites is less pronounced than that of pure poly(PCDA) might result from the relatively high rigidity of the conjugated backbone of the composites. As mentioned above, due to the interaction between carboxyl groups and metal ion (tethering 2), the size mismatch between the metal ion and the alkyl chain restricts close packing of the alkyl chains. The restriction result in tensions in the packing structure of the alkyl chains, as indicated by the weak and wide signal in the XRD patterns. The tension will be conveyed to and thus distort the resultant polydiacetylene backbone; it is imaginable that the tension should also enhance the rigidity of the conjugated backbone. From another perspective, the composites have longer ECLs than pure poly(PCDA) (as indicated by the 30 nm red-shift of the maximum UV-vis absorption relative to pure poly(PCDA)). The longer ECLs implicate higher rigidities of the conjugated backbones of the composites, because the backbones have to be more rigid to resist bigger entropy disturbances.

References

- (1) X. Huang, S. Jiang and M. Liu, *The Journal of Physical Chemistry B*, 2005, **109**, 114-119.
- (2) S. Wu, L. Pan, Y. Huang, N. Yang and Q. Zhang, *Soft Matter*, 2018, **14**, 6929-6937.
- (3) A. Demartini, M. Alloisio, C. Cuniberti, G. Dellepiane, S. A. Jadhav, S. Thea, E. Giorgetti, C. Gellini and M. Muniz-Miranda, *The Journal of Physical Chemistry C*, 2009, **113**, 19475-19481.
- (4) S. J. Varma, J. Kumar, Y. Liu, K. Layne, J. Wu, C. Liang, Y. Nakanishi, A. Aliyan, W. Yang and P. M. Ajayan, *Advanced Optical Materials*, 2017, **5**, 1700713.
- (5) J. S. Filhol, J. Deschamps, S. G. Dutremez, B. Boury, T. Barisien, L. Legrand and M. Schott, *Journal of the American Chemical Society*, 2009, **131**, 6976-6988.