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Shedding light on hidden reaction pathways in radical polymerization by a porous coordination network[†]

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A coordination network comprising 2-vinyltriphenylene was treated with AIBN at a high temperature, but the radical polymerization of the vinyl monomer was completely suppressed by spatial separation and otherwise hidden aerobic oxidation pathways are enhanced.

Radical initiated reactions often lead to a complicated mixture that hampers selective synthesis of desired products and detailed mechanistic study. Above all, when a rapid polymerization reaction takes place, it becomes increasingly difficult to isolate and characterise minor products that yet give important insights for synthetic and mechanistic studies. Investigation of such obscure reaction pathways has been conventionally performed under low concentration of monomers or in the presence of suitable inhibitors, but these unusual reaction conditions often entirely change the course of target reactions. We envisioned that the spatial separation of monomers would effectively inhibit polymerization, thus showing up hidden reaction pathways. Porous coordination networks¹⁻⁵ are capable of aligning guest molecules within a three-dimensionally ordered crystalline framework, while providing the pores with solution-like fluidity. While the polymerization of guests in pores has been extensively investigated,^{6,7} it is rare to utilize coordination networks for preventing oligomerization of monomers.⁸ Herein, we use a porous coordination network as a new scaffold to suppress the radical polymerization of vinyl monomer 1 even at high local concentration and in the presence of a radical initiator, 2,2'-azobis(isobutyronitrile) (AIBN). As a case study, AIBN-initiated oxidation of 1 with molecular oxygen, which is an undesired but mechanistically important side reaction to decrease the degree of polymerization, was investigated in the network complex.

A porous coordination network which intercalates 2-vinyltriphenylene (1) was synthesized by the layer diffusion of a methanolic solution of ZnI₂ onto a solution of 1 and tris(2,4,6-pyridyl)triazine (2) in nitrobenzene/methanol (Scheme 1). Crystallization at room temperature in the dark for 1 week gave yellow needle-like crystals in 50% yield. The averaged formula of the as-synthesized network 3 was determined to be $[(ZnI_2)_2(2)_3(1) \cdot (C_6H_5NO_2)_4]_n$ on the basis of elemental analysis.[‡] X-Ray crystallographic analysis revealed that the network structure of 3 is isomorphous to previously reported networks.⁹⁻¹¹ Alternating π - π stacking of aromatic guest 1 and ligand 2 forms columnar structures parallel to the *b*-axis. The vinyl substituent of **1** pointed into the rectangular pores (7.4 Å \times 5.5 Å), allowing direct interactions with incoming guest molecules. More importantly, each vinyl substrate 1 is spatially well-isolated within 3: the closest centreto-centre distances between neighbouring two vinyl groups are 6.6 Å (within a single column) and 10.2 Å (between adjacent two columns) (Fig. 1). From the volume of the unit cell, the local concentration of 1 in crystal is estimated to be 0.77 M.



Fig. 1 (a) Crystal structure of network **3** viewing along the *b*-axis. (b) Columnar π -stacks of 2-vinyltripheynlene (1) and ligand **2** highlighted with a red square in (a). (c) Spatial arrangement of eight guests **1** in the unit lattice.

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Tokyo, 113-8656, Japan † Electronic supplementary information (ESI) available: Experimental details and spectroscopic data. CCDC 838868. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/ c1cc15053g



Scheme 1 Synthesis of coordination network 3.

We found that, under thermal and radical conditions, the polymerization of guest 1 was completely suppressed within network 3. We first exposed network 3 to standard polymerization conditions for styrene monomers; crystals of 3 were heated to 80 °C in cyclohexane in the presence of AIBN (3 mol% to monomer 1) for 1 d under an Ar atmosphere. Then crystals were filtered, and intercalated triphenylene guests were extracted with CH₂Cl₂ after decomposing crystals with THF/water. As we expected from the crystal structure, 2-vinyltriphenylene (1) was quantitatively recovered.¹² We also conducted a similar reaction with a large excess amount of AIBN (ca. 12 equiv. to 1), yet ¹H NMR and HPLC analyses revealed that no polymeric products formed within the pores of 3 (Fig. 2a). Besides 1, AIBN and its pyrolytic product, 2,2,3,3-tetramethylsuccinonitrile, were found in the reaction mixture extracted from crystals, which indicated the penetration of the radical initiator into the pores.¹³ It is also notable that guest **1** in network **3** underwent neither polymerization nor cyclodimerisation even under UV irradiation by a Hg lamp.

Based on the above results, we next examined the AIBNinitiated reaction of network-embedded **1** with molecular oxygen (Scheme 2). When the crystals of **3** were treated with AIBN solution under aerobic conditions for 1 d, 2-formyltriphenylene (**4**) and epoxide **5** were obtained in 7 and 20% yield, respectively (Fig. 2b and Fig. S1 in ESI†). This reaction was not accompanied by polymerization and thus unreacted **1** was fully recovered. The oxygenated products **4** and **5** can be detected even in the reaction mixture after polymerization in solution, but their yields are quite low (<1%) (Fig. 2c).¹⁴



Fig. 2 HPLC chromatograms of the products from the reactions of styrene derivative **1** and AIBN: (a) in crystals **3** under Ar, (b) in crystals **3** under aerobic conditions, and (c) in solution under aerobic conditions. (*denotes an impurity signal which derives from epoxide **5** formed under the measurement conditions.)



Scheme 2 AIBN-initiated reactions of vinyl monomer 1 in network crystal 3 and in solution.

The formation of oxygenated products **4** and **5** are attributable to radical reactions with molecular oxygen. It is known that thermolysis of AIBN in the presence of oxygen gives rise to 2-cyano-2-propylperoxyl and 2-cyano-2-propyloxyl radicals, which can react with olefins to yield epoxide and carbonyl compounds.^{15,16} Nevertheless, these oxidation pathways are considerably slower than polymerization under relatively high concentration of vinyl monomer **1** and cannot be major reaction pathways. It is therefore noteworthy that coordination network **3** selectively suppressed the polymerization by spatial separation, while making dominant the hidden radical oxidation pathways.

In conclusion, we have synthesized a porous coordination network **3** in which radical polymerization of styrene derivative **1** is completely inhibited since the guest molecules are spatially well-separated with regular intervals. Yet, guest **1** is still capable of reacting with radical species in the pores, thus predominantly forming oxygenated products **4** and **5**. We believe that our coordination network is a new crystalline-state reaction container that makes it possible to analyze complicated reaction pathways, to reveal unknown mechanisms, and, even better, to find synthetically useful reactions.

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Notes and references

‡ Crystal data for 3: C₅₆H₃₈I₆N₁₂Zn₃, M = 1836.56, orthorhombic, a = 27.574(3) Å, b = 13.8942(17) Å, c = 44.874(6) Å, $\alpha = \beta = \gamma = 90^{\circ}$, V = 17192(4) Å³, T = 90(2) K, space group *Pbca*, Z = 8, 171751 reflections measured, 17586 independent reflections ($R_{int} = 0.0509$). The final R_1 value is 0.0804 ($I > 2\sigma(I)$). The final w $R(F^2)$ value is 0.2084 (all data), CCDC 838868. The SQUEEZE program in PLATON was used for analysis to remove the disordered solvent densities in the pores.

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- 12 Very minor peaks (less than 1% based on integration ratio) presumably due to adducts of 2-cyano-2-propyl radical were observed in the ¹H NMR (Fig. S2, ESI[†]).
- 13 We confirmed that compound 1 readily polymerizes in solution; when a 0.40 M C₆F₆ solution of 1 was treated with 3 mol% of AIBN at 80 °C,

poly-1 with a number-average molecular weight (M_n) of 2.12×10^4 (based on polystyrene standard) was obtained, despite the remarkably smaller concentration of 1 in the solution than in network 3.

- 14 We examined the radical polymerization of **1** under aerobic conditions and observed the formation of poly-**1** with the degree of polymerization ($M_n = 1.21 \times 10^4$) in 88% conversion yield. Only trace amounts of **4** and **5** (less than 1% each) were detected after the reaction (Fig. 2c).
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