Oscillations, traveling fronts and patterns in a supramolecular system

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Supramolecular polymers such as microtubules operate under non-equilibrium conditions to drive crucial functions in cells such as motility, division and organelle transport.[1] In vivo and in vitro size oscillations of individual microtubules[2,3] (dynamic instabilities) and collective oscillations[4] have been observed. In addition, dynamic spatial structures like waves and polygons can form in non-stirred systems.[5] Here we describe an artificial supramolecular polymer made of a perylene diimide derivative that displays oscillations, traveling fronts, and centimetre-scale self-organized patterns when pushed far from equilibrium by chemical fuels. Oscillations arise from a positive feedback due to nucleation-elongation-fragmentation, and a negative feedback due to size-dependent depolymerisation. Traveling fronts and patterns form due to self-assembly induced density differences that cause system-wide convection. In our system, the species responsible for the non-linear dynamics and those that self-assemble are one and the same. In contrast, other reported oscillating assemblies formed by vesicles[6], micelles[7], or particles[8] rely on the combination of a known chemical oscillator and a stimuli-responsive system, either by communication through the solvent (e.g., by changing pH[7–9]), or by anchoring one of the species covalently (e.g., Belousov-Zhabotinsky catalyst[6,10]). Designing self-oscillating supramolecular polymers and large scale dissipative structures bring us closer to create more life-like materials[11] that respond to external stimuli similarly to living cells, or to create artificial autonomous chemical robots.[12]

We use a perylene diimide derivative **PDI** that forms supramolecular polymers in aqueous borate buffer (Figure 1a). Upon reduction by $Na_2S_2O_4$ the dianion **PDI^{2-}** is mostly monomeric, and at equilibrium with small ~100 nm **PDI^{2-}** assemblies (see below).[13] Oxidation by atmospheric oxygen leads first to the radical anion **PDI$^{•-}$**, before returning to the neutral **PDI$_{mon}$** (see Methods). The latter undergoes a cooperative supramolecular polymerisation to form micron-sized colloidal assemblies **PDI$_{assem}$** by side-to-side bundling of one-dimensional **PDI** fibers.[13] The polymerisation process can be followed by UV-Vis spectroscopy where a characteristic band at 528 nm can be tracked, colour camera where pink / blue / purple corresponds to **PDI / PDI$^{•-}$ / PDI^{2-}** respectively, or dynamic light scattering (Supplementary Figures 1 and 2).

The cooperative nature of the assembly process is discerned from the sigmoidal time progression of the degree of polymerisation α vs. time (Figure 1c), where $\alpha = 0$ corresponds to the disassembled state and $\alpha = 1$ to the fully assembled state. Light scattering shows a similar sigmoidal increase from ~100 to 1500 nm in hydrodynamic radius R_H during assembly (Supplementary Figure 3, black line). In addition, the fact that the half-time τ scales as $\log(\tau) \propto -0.48 \log(C_0)$, where C_0 is the initial concentration of **PDI**, indicates that more processes are occurring than only nucleation and elongation (Supplementary Section 2 and Supplementary Figure 4). A detailed analysis including seeding experiment and global fitting by analytical models[14] showed that fragmentation is also involved (Figure 1c, Supplementary Section 2). Fragmentation was further confirmed by performing experiments at different stirring / shear rates, where the fastest growth was observed at the highest rate (cf. Supplementary Figure 7). Others have shown that stirring can lead to fragmentation[15] or increased secondary nucleation[16].

The reduction rate of **PDI$_{assem}$** was quantified using stopped-flow experiments, where a solution of reductant $Na_2S_2O_4$ was rapidly mixed with **PDI$_{mon}$** solutions that had been aged for determined times. Solutions prepared from freshly synthesized **PDI** powder gave seemingly random reduction kinetic profiles, due to the broad distribution[13] of particle sizes. Therefore, all solutions were first fully reduced to **PDI^{2-}**, and stirred in air until a bright pink colour of the neutral **PDI$_{mon}$** was observed. The latter solution was rapidly transferred into the stopped-flow syringe and left to age. Figure 1d shows a typical reduction experiment tracked using the **PDI^{2-}** absorption

band at 612 nm, which shows first a fast exponential increase up to ~1 s, followed by a slower sigmoidal increase. These complicated kinetics can be understood by a 2-step process: 1) a first-order reaction where $Na_2S_2O_4$ reacts with the outer shell of the **PDI**$_{assem}$ colloidal assemblies leading to a rapid colour / absorption change (i in Fig. 1b), and 2) surface-erosion of the colloids leading to sigmoidal release[17] of **PDI** into solution followed by instantaneous reduction to **PDI**$^{2-}$ (ii–iv in Fig. 1b). The time constants corresponding to these two processes (τ_1 and τ_2, respectively) both increase by a factor 2–3 over the 90 min aging period (cf. insets in Figure 1d). In other words, during the **PDI**$_{mon}$ to **PDI**$_{assem}$ aging the assemblies are getting larger and larger (from ~100 nm to ~2 μm, cf. Supplementary Section 1), leading to ever slower apparent reduction rates.

So far, we have shown that there is significant non-linearity in both the assembly and disassembly kinetics of **PDI** structures. The nucleation-elongation-fragmentation process acts as a positive feedback mechanism, whereas the size-dependent reduction / disassembly of **PDI** can be seen as a negative feedback; both of which are thought to be required[18] to obtain emergent properties such as oscillations. With the basic elements to construct an oscillator in place we set out to find the oscillating window by pushing the system far from equilibrium in a stirred semi-batch reactor.

Practically, we placed a stirred glass vial in a well-ventilated box with constant oxygen supply and illumination and used a syringe pump to inject the reductant ($Na_2S_2O_4$) solution continuously (Figure 2a). A fast diode-array UV/Vis detector, colour CCD camera, near infra-red static light scattering IR-SLS, and confocal microscopy were used for analysis (Supplementary Section 3 and 4). Conventional visible light scattering cannot be used, since 1) **PDI**$^{2-}$ absorbs the 639 nm laser light, preventing quantitative static light scattering (cf. Supplementary Figure 3), and 2) stirring disrupts the correlation needed for dynamic light scattering. A home-built 905 nm IR-SLS setup was used instead (Supplementary Figure 9); to benchmark the setup we performed a step-wise redox cycle (Supplementary Figure 10), namely: i) a solution of **PDI**$_{assem}$ has significant IR-SLS intensity and a pink colour, ii) addition of reductant leads to **PDI**$^{2-}$ and a fast drop of the colour intensity of the red and blue channel, iii) oxidation in air to **PDI**$^{\bullet-}$ results in a local maximum in blue intensity, iv) further oxidation to **PDI**$_{mon}$ restores the initial pink solution colour while the IR-SLS intensity reaches a minimum, v) assembly into **PDI**$_{assem}$ leads to a sigmoidal increase in scattering and visual turbidity. The latter experiment shows that reduction leads to disassembly and low IR-SLS intensity, and that **PDI**$_{mon}$ is the least assembled state consisting of ~100 nm structures.

The phase space of the system was explored in the semi-batch reactor by varying the initial concentration of **PDI** vs. the flow rate of reductant (Figure 2b). In all cases, the initial solution was completely reduced to **PDI**$^{2-}$ before starting the continuous inflow of reductant. The composition of the solution species **PDI**$^{2-}$ / **PDI**$^{\bullet-}$ / **PDI**$_{mon}$ / **PDI**$_{assem}$ was determined from colour analysis and UV/Vis spectra (see supplementary section 3). For low flow rates a steady state 'SS' was observed by following the red channel of the CCD camera (Figure 2b,c). The composition of the solution is close to fully neutral assembled **PDI**, apparent from the solution colour and UV-Vis spectrum. To confirm the latter, the reductant inflow was stopped, causing full oxidation and assembly into **PDI**$_{assem}$, and leading only to a minor (< 5 %) increase in intensity (Supplementary Figure 11a). Increasing the flow rate further, leads to complex oscillations in a narrow window 'OSC' (Figure 2b,d, Supplementary Video 1). For the highest flow rates, precipitation 'PR' occurred after ~40 min, where a film of solids would accumulate at the solution/air interface (Figure 2b,e).

Oscillations were always damped and with seemingly period-2 characteristics. That is, oscillations occur in 'pairs', where one of the two peaks is lower than the other (cf. Figure 2d). The amplitude of the oscillations gradually decreases, whereas their frequency is ever increasing. The path to oscillations can be understood by looking at the colour space in two-dimensions (Figure 2f). To this end, the red / green / blue channels obtained from the camera are converted to CIE 1931 x and y colour coordinates. In Figure 2f the process is as follows: i) reduction of **PDI** solution to **PDI**$^{2-}$ by addition of an aliquot of $Na_2S_2O_4$ solution; ii) atmospheric air oxidizes to **PDI**$^{\bullet-}$ until very small **PDI**$_{mon}$ structures are formed; iii) sigmoidal growth to large assemblies **PDI**$_{assem}$; iv) start of the continuous flow of reductant, followed shortly by oscillations; v) damping and decay of oscillations. To be sure that oscillations in the size of the assemblies occurred, we performed experiments combining IR-SLS with colour tracking (Figure 2g and Supplementary Figure 12). In Figure 2g one can see that during a large oscillation all the way to disassembled **PDI**$^{2-}$ (index ii), the IR-SLS intensity drops to the baseline and the (red) colour intensity is low as well; shortly thereafter, neutral **PDI**$_{mon}$ is formed (index iii) leading to rapid increase in colour intensity, followed by a much slower sigmoidal increase in IR-SLS intensity and visual turbidity in the vial (index iv).

121 A subsequent oscillation shows a similar trend (cf. indices v–viii in Figure 2g). Further evidence
122 comes from confocal microscopy, where aliquots were taken during oscillations showing nearly
123 complete disappearance of colloidal assemblies during large oscillations (e.g., compare v and vi
124 in Supplementary Figure 13).
125   In general, many oscillators studied under semi-batch conditions show damped
126 oscillations due to accumulation of waste products. Microtubules for example, suffer from
127 increasing concentrations of guanosine diphosphate over their triphosphate analogue, which is
128 thought to lead to amplitude loss in batch experiments.[20,21] To test whether waste accumulation
129 was of importance in our system, we added an equivalent of 5 hours of waste mid-way during
130 oscillations (Supplementary Figure 14a). Only a very minor disturbance in the oscillations was
131 observed. As a negative control, an aliquot of buffer of the same volume as in the 'waste addition
132 experiments' was added, which did not disturb the oscillations (Supplementary Figure 14b). From
133 the latter two series of experiments we conclude that waste accumulation or resulting changes in
134 ionic strength are not responsible for the damping of the oscillations. Another salient detail is that
135 oscillations can never be obtained when starting from aged **PDI$_{assem}$** solutions, but only when
136 starting from mostly disassembled **PDI$_{mon}$** solutions (i.e., by fully reducing to **PDI^{2-}**, and then
137 oxidizing to **PDI** before starting inflow of reductant). In other words, the oscillations are inherently
138 transient and 'en route' to a non-oscillating state consisting of large **PDI$_{assem}$**. The latter is also
139 confirmed by the model we develop (see below).
140   To understand the oscillator behaviour, we expanded a recent nucleation-elongation-
141 fragmentation model[19] (used above, cf. Figure 1c) with chemically-fuelled reduction by $Na_2S_2O_4$
142 and oxidation by O_2. Specifically, we consider reduction of a polymer Q_j of length j (i.e., the
143 removal of an end-capped monomer from a one-dimensional polymer and its instantaneous
144 reduction), and oxidation of non-assembled reduced monomer R to monomer O. Since both **PDI$^{•-}$**
145 and **PDI^{2-}** are mostly disassembled (cf. Supplementary Figure 2), we combine them both into
146 reduced monomer R. Figure 3a shows the used equations, rate constants, and schematic
147 representations of the model. Using the mathematical approach by Knowles and co-workers[19] we
148 derived the following equations (cf. Supplementary section 5) for the number concentration of
149 polymers [P], the mass concentration of polymers [M], and the concentrations [O] and [R] of the
150 monomer species:
151
152 $\frac{d[P]}{dt} = -3k_{frag}[P] + k_{frag}[M] + k_{nuc}[O]^2,$ (1)
153 $\frac{d[M]}{dt} = -2(k_{frag} + k_{red})[P] + 2k_{el}[P][O] + 2k_{nuc}[O]^2,$ (2)
154 $\frac{d[R]}{dt} = k_{red}[P] - k_{ox}[R],$ (3)
155 $[O] = [m]_{tot} - [M] - [R],$ (4)
156
157 where we have used nucleus size $n = 2$ and conserve the total mass $[m]_{tot}$. A continuation analysis
158 and simulations of the model were performed with MatCont (see Supplementary Section 5). The
159 main finding is that damped oscillations can be observed in all variables (total number of
160 polymers, total mass of polymers, and the monomer concentrations) for an extended range of
161 parameters (cf. Figure 3b and Supplementary Figure 15). We classify the behaviour as oscillating
162 if the amplitude within 3 consecutive oscillations is larger than 50% of the asymptotic steady state
163 value of [M]. A number of aspects of the model are in qualitative agreement with the experiments.
164 One can compare Figure 3b to 2b (see above), where in the former at low flow rate of reductant
165 a steady-state SS is obtained, and in the latter analogously at low k_{red} a SS is found (note: k_{ox} in
166 the experiments is always constant, and determined by influx of atmospheric oxygen). In other
167 words, at low rates of reduction the molecules stay in the assembled **PDI$_{assem}$** state, as one would
168 expect. Increasing k_{red} values leads to damped oscillations (OSC in Figure 3b), since there is a
169 competition between assembled and disassembled **PDI** with non-linear kinetics. The top inset in
170 Figure 3b shows time traces along a vertical phase line, where decreasing k_{ox} leads to more
171 oscillations (i.e., less damping), an increasing asymptotic value, and an increasing period. A
172 similar trend is seen for the horizontal phase line (bottom inset Figure 3b) in the direction of
173 increasing k_{red} at constant k_{ox}. For too large k_{red} the oscillations become unstable and lead to
174 unphysical (negative and extremely large) concentrations, shown in the 'US' region in Figure 3b.
175 Surprisingly, this is where in experiments precipitation is observed (Figure 2b), though a direct
176 comparison cannot be made at this point.
177   Other than the chemically fuelled rates constants k_{ox} and k_{red}, fragmentation k_{frag} is a
178 sensitive parameter; decreasing its value leads to a decrease in damping (Figure 3c), allowing
179 hundreds of oscillations up to the point that experimentally it would be difficult to distinguish from

180 sustained oscillations. More generally, we can vary the nucleation k_{nuc}, and elongation k_{el} rates
181 and conserve the qualitative finding—that is, the oscillations are generic. If the initial condition
182 contains enough polymers, the nucleation rate can even be set to zero, while maintaining the
183 oscillations.
184 Beyond oscillations, we investigated the spatiotemporal behaviour of our supramolecular
185 system. Firstly, we explored traveling fronts, where a **PDI$_{mon}$** solution was seeded with preformed
186 1h old **PDI$_{assem}$** polymers, leading to isothermal frontal supramolecular polymerisation in adjacent
187 volumes (Figure 4a,b, and Supplementary Video 2). Temperature differences are not important
188 in our system as they would quickly equalize due to fast thermal diffusion.[22] In a rectangular chip
189 with two parallel glass slides spaced by 1 mm, a traveling front with an initial velocity of 0.26 ±
190 0.01 mm min^{-1}—about ~20 times faster than ~100 nm **PDI$_{mon}$** diffusion—can be seen that
191 increases the area initially occupied by the seeds (cf. left panel of Figure 4b and Supplementary
192 Video 2). Later on, a ring structure is formed that slows down progressively until it stops
193 completely, as can be seen in the kymograph in Figure 4c. Upon closer inspection of the traveling
194 front using confocal microscopy and analysis by particle image velocimetry, it was clear that large
195 scale in-plane convection was present in the chip, shortly after seeds were added (Supplementary
196 Video 3). As a control, we added **PDI$_{assem}$** and buffer to the same **PDI$_{mon}$** solution, and observed
197 much more spreading of the seeded front vs. the non-seeded region (Supplementary Video 4). In
198 other words, seeding triggers the convective front, similarly to (thermal) initiation in covalent
199 frontal polymerisation.[23] **PDI$_{mon}$** solutions have an ~0.2% higher density as compared to fully
200 assembled **PDI$_{assem}$** (Supplementary Figure 16). While this seems like a small difference, it is
201 known that in a horizontal experiment, neighbouring volumes with different density always lead
202 to convective instabilities.[22] The traveling front progressively slows down (Figure 4c), since
203 spontaneous nucleation and growth occurs in the unreacted zones over time as well, reducing
204 the density difference with the front, and thus halting convection.
205 When replacing the top glass plate with mineral oil, convection is exacerbated and a
206 single massive convection cell is formed (Figure 4d). In the latter experiment, **PDI^{2-}** is oxidized by
207 atmospheric oxygen diffusing through the oil, leading to an outward moving propagating oxidation
208 front (cf. dashed area, Figure 4d), while simultaneously turning the entire volume into a single
209 convection cell leading to alignment of **PDI$_{assem}$** structures along the flow lines (Supplementary
210 Video 5). Small scale convection is observed in unseeded as well as seeded experiments (far
211 from the front), where mosaic structures are formed (Figure 4e and Supplementary Figure 17).
212 Similar structures have been observed in microtubule experiments[5] and in an inorganic system[24].
213 Again, spontaneous nucleation and growth leads to small zones of different composition and
214 density, inducing localized structures.
215 We have shown collective size oscillations in a supramolecular polymer system by
216 combining cooperative self-assembly with chemically fuelled disassembly. Interestingly, our
217 model shows that non-linear negative feedback like we have observed experimentally (i.e., size-
218 dependent reduction / disassembly rates, see above) is not required; positive non-linear feedback
219 from the supramolecular polymerisation combined with chemically-fuelled linear depolymerisation
220 is sufficient to obtain oscillations. This provides an exciting outlook for other supramolecular
221 polymers reported on so far,[25–29] which use chemical fuels to drive (seemingly) cooperative
222 polymerisation. The type of supramolecular oscillations we find here are always damped. This is
223 because they are found close to a subcritical Hopf bifurcation,[30] which leads to an unstable limit
224 cycle and therefore does not support sustained oscillations. Similar observations have been made
225 in microtubule systems, where inherent damping was suggested as well.[31] Other than temporal
226 order, we have shown spatiotemporal phenomena. In non-stirred experiments cm-scale
227 polymerization fronts and polygonal convection patterns are formed due to density differences
228 between assembled and non-assembled regions. The latter polygons are *dissipative structures*
229 in the Prigogine-sense, meaning they are only observed beyond stability of the thermodynamic
230 branch.[32] Recognizing dissipative structures in supramolecular systems is difficult, since order
231 can already exists at equilibrium due to non-covalent interactions. Dissipative structures,
232 however, occur at length-scales much larger than the molecules and their fundamental
233 (intermolecular) interactions, and should disappear if the system were to be isolated. Our system
234 has nm–µm scale order at the level of the supramolecular structures, as well as cm-scale order
235 at the level of the dissipative (convective) structures. It will be interesting to further explore the
236 interplay of out-of-equilibrium supramolecular polymerisation with convective instabilities, in
237 addition to recent enzymatic convection patterns[33] and supramolecular–mechanical
238 couplings[34,35]. This will allow large scale self-organization, transport, and communication driven
239 by fuelled dissipative non-equilibrium self-assembly[36]. In general, non-equilibrium supramolecular

240 polymerization[36,37] only leads to large scale emergent properties such as oscillations when the
241 system is pushed far from equilibrium beyond the first bifurcation.
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244 **Data availability.** The data that support the plots within this paper and other findings of this study are
245 available from the corresponding authors upon reasonable request.
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248 **References**
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Author contributions

J.L.–I. and T.M.H. designed and performed the experiments, and analysed data. J.L.–I. performed the synthesis. A.T. performed static and dynamic light scattering experiments. A.T. and T.A. developed near-infra red static light scattering and interpreted the results. J.L.–I., A.T. and T.A. carried out the NIR static light scattering experiments. M.S. and T.M.H. performed modelling and interpretation of the results. J.L.–I. and T.M.H. wrote the paper. All authors discussed about the results, and commented on the manuscript. T.M.H. conceived the overall project and supervised the research.

Competing interests

The authors declare no competing interests.

Additional Information

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Figure Captions

Fig. 1. Kinetics of redox fuelled PDI assembly and disassembly. a, **PDI** is reduced to **PDI**$^{2-}$ upon addition of $Na_2S_2O_4$. Spontaneous oxidation in air leads first to radical anion **PDI**$^{\bullet-}$ and then to neutral **PDI**. **b**, After one redox cycle (i.e., reduction to **PDI**$^{2-}$ and oxidation to **PDI$_{mon}$**, k_{red} and k_{ox}, respectively), **PDI$_{mon}$** grows via a cooperative polymerisation mechanism with nucleation k_{nuc}, elongation k_{el}, and fragmentation k_{frag} constants. The system is also characterized by a size-dependent reduction rate for **PDI$_{assem}$** ($k_{red,p}$, see data in panel d). **c**, The degree of polymerisation α as a function of time at different seeding per cent and **PDI** concentrations (see methods). Global fitting was used (solid lines) with a saturating elongation + fragmentation model[14,19] yielding: k_{nuc} = 0.069 ± 0.002 M^{-1} min^{-1}, k_{el} = 4.5•10^6 ± 4•10^5 M^{-1} min^{-1}, k_{frag} = 2.38•10^{-5} ± 2.8•10^{-6} min^{-1}, K_e = 1.80•10^{-5} ± 1.5•10^{-6} M, nucleus size n = 2 and error MRE = 0.0015. **d**, Reduction kinetics followed by stopped-flow where 80 μL of a 100 μM **PDI$_{mon}$** solution and 80 μL of a 50 mM $Na_2S_2O_4$ solution were loaded in syringes and quickly mixed at defined intervals. Over time **PDI$_{mon}$** grows to **PDI$_{assem}$** in the syringe, leading to slower kinetics shown in the insets. Two processes are observed: one exponential with time constant τ_1 and one sigmoidal with constant τ_2, which increase over time (see main text and methods). The red dashed line indicates the transition between the two processes. The reduction kinetics were followed at the characteristic dianion bands of **PDI**$^{2-}$ at 612 nm.

Fig. 2. Supramolecular oscillations. a, Three different states (steady state **SS**, oscillations **OSC**, and precipitation **PR**) were observed in a semi-batch reactor under continuous influx of chemical fuel ($Na_2S_2O_4$).

b, The phase space of **PDI** concentration vs. flow rate of Na$_2$S$_2$O$_4$. **c,d,e,** The different states of a 100 μM **PDI** solution are shown (only the red channel intensity is shown for simplicity), **c**, a first steady state (**SS**) can be kept at low flow rates in which mostly neutral **PDI** is observed. **d**, oscillations (**OSC**) were observed by increasing the flow rate. **e**, higher flow rates lead to a state with mostly **PDI**$^{2-}$ where precipitation (**PR**) occurs after ~40 min. **f**, CIE 1931 coordinates (x, y) coding for the red, green and blue channels. See the main text for a description of the indices i–v. **g,** Scattering intensity (left axis, black line) and red colour intensity (right axis, red line) of **PDI** (i, t = 20 min) vs time during two oscillations. The decrease of the scattering and red channel intensity indicates the formation of **PDI**$^{•-}$ and **PDI**$^{2-}$ species (ii, t = 25 min, and v, t = 38 min) and a mostly disassembled state. Oxidation leading to **PDI$_{mon}$** is apparent from the increase of the red channel intensities and pink color (iii, t = 34 min and vi, t = 42 min). Self-assembly of **PDI$_{mon}$** into **PDI$_{assem}$** leads to an increase in scattering intensity and visible turbidity in the solution (iv, t = 36.3 min, and vii, t = 48 min, and viii, t = 59 min). See Supplementary Video 1.

Fig. 3 Supramolecular oscillator model. a, The nucleation-elongation-fragmentation model is expanded with chemical fuels, i.e., reduction to **PDI**$^{•-}$ or **PDI**$^{2-}$ species R and the oxidation back to **PDI$_{mon}$** species (here O). **b**, Phase space plot as a function of the reduction and oxidation rates (k_{red} and k_{ox}, respectively) shows three different states: steady-state 'SS', oscillations 'OSC' and unphysical solutions 'US'. The top inset corresponds to the vertical cut through the oscillating window 'OSC' (along the solid line). The bottom inset shows the horizontal cut (along the dashed line). Initial conditions: $[P] = 1 \cdot 10^{-8}$ M, $[M] = 1 \cdot 10^{-7}$ M, $[R] = 5 \cdot 10^{-6}$ M, $[m]_{tot} = 1 \cdot 10^{-5}$ M; constants: $k_{frag} = 3 \cdot 10^{-4}$ s^{-1}, $k_{nuc} = 4 \cdot 10^{-4}$ M^{-1} s^{-1}, $k_{el} = 400$ M^{-1} s^{-1}. **c**, Reduced damping for smaller values of k_{frag} up to the point of nearly sustained oscillations (black line).

Fig. 4. Supramolecular traveling fronts and patterns. a, A rectangular 3D printed chip (50 x 25 mm) with two parallel glass slides spaced by 1 mm was used. A **PDI$_{mon}$** solution was immediately injected into the chip. Then, **PDI$_{assem}$** seeds (30 μL of a 1h old **PDI$_{mon}$** solution) were added from one side of the chip. **b,** A traveling front in adjacent volumes was observed using a colour CCD equipped stereoscope (cf. Supplementary Video 2). The brightness/contrast has been increased to better show the front. **c**, The kymograph shows the progressive decrease in velocity of the front (extracted from Supplementary Video 2). **d**, The top glass cover slide was replaced by mineral oil permitting diffusion of O$_2$ and near-frictionless fluid transport. A **PDI**$^{2-}$ solution (100 μM) was poured into the chip and covered by oil. An outward moving front (dashed area) was observed showing oxidation to **PDI$_{mon}$**. Simultaneously, a single massive convection cell is formed leading to an alignment of **PDI$_{assem}$** structures in the direction of the flow (see Supplementary Video 5). **e**, Transient formation of polygons (appearing after ~ 30 min) was observed while performing propagating front experiments with identical conditions to those as shown in panel **a**.

Methods

PDI system. PDI was synthesized according to our protocol described recently.[13] In short, **PDI** was prepared by imidization of perylene-3,4,9,10-tetracarboxylic acid dianhydride with ethylenediamine. Afterwards, amide coupling between the perylene diimide derivative and oligoethyleneglycol derived from gallic acid was performed yielding the target compound **PDI**.

Preparation of PDI$_{mon}$. A 100 μM **PDI** mother solution was prepared by dissolving **PDI** (1 mg, 0.60 μmol) in 50 mM borate buffer, pH 8. **PDI** solution (2 mL) was reduced to mostly monomeric **PDI**$^{2-}$ by adding 2 μL of a 400 mM Na$_2$S$_2$O$_4$ solution (in borate buffer) under constant stirring (i.e., 1000 rpm). Spontaneous oxidation in air (O$_2$) leads to **PDI**$^{•-}$ and then to **PDI$_{mon}$**. Afterwards, **PDI$_{mon}$** grows via a cooperative polymerisation mechanism yielding colloidal **PDI$_{assem}$**.

Dynamic light scattering (DLS). The intensity autocorrelation functions $g^{(2)}(q,\tau) \equiv \langle I(q,0)I(q,\tau)\rangle / \langle I(q,0)^2 \rangle$ were measured on a home-built light scattering setup with an ALV7002 digital correlator using a laser diode at $\lambda = 639$ nm at a wavevector $q = 0.0185$ nm^{-1} (90° scattering angle). Measurements were performed on 100 μM **PDI**, **PDI**$^{•-}$ and **PDI**$^{2-}$ every 60 s for 10 min. The relaxation dynamics were analysed by the inverse Laplace transformation $g^{(1)}(\tau) = \int_0^\infty H(\Gamma)e^{-\Gamma t}d\Gamma$ where $g^{(1)} = \sqrt{g^{(2)} - 1}$. Hydrodynamic radii R_H were then calculated using the Stokes-Einstein relation $R_H = k_B T/(6\pi\eta D)$ where $D = 1/(\tau q^2)$ and the root mean-squared deviation from the mean size of each state where determined fitting the hydrodynamic radius distribution with a Schultz distribution function. In order to perform the cooperative growth analysis of **PDI$_{mon}$** (cf. Supplementary Figure 3), the intensity autocorrelation functions were fitted with a monoexponential decay function $g_1(t) = e^{-\Gamma t}$.

Kinetics of the cooperative polymerisation. A 100 μM **PDI** mother solution was prepared by dissolving **PDI** (1 mg, 0.60 μmol) in 50 mM borate buffer, pH 8. The different concentrations (i.e., 75, 50 and 25 μM) were prepared by diluting the mother solution with the corresponding amount of borate buffer solution in order to yield the desired concentration. Afterwards, 2 mL of each **PDI** solution was reduced by adding 2 μL of a 400 mM Na$_2$S$_2$O$_4$ solution (in borate buffer) at constant stirring rate (i.e., 1000 rpm). Spontaneous oxidation in air leads to **PDI$_{mon}$** species. A 100 μM freshly oxidized **PDI$_{mon}$** solution (1 mL) was aged for 1 h

438	in order to prepare **PDI$_{assem}$** seeds. Seeding experiments were performed by adding different amounts of
439	seeds (i.e., 15, 10 and 5 % in v/v) to a 100 μM **PDI$_{mon}$** solution (final volume of the solution was 2 mL).
440	Stirring experiments were performed on a 100 μM **PDI$_{mon}$** solution (2 mL) at different stirring rates (i.e., 1000,
441	750 and 500 rpm). Kinetics experiments were performed on a JASCO V-670 spectrophotometer equipped
442	with a Peltier system as a temperature controller. Spectra (i.e., from 400 to 700 nm) were recorded in a 1
443	cm quartz cuvette at 25 ºC.
444	
445	**Reduction kinetics.** The reduction kinetics of **PDI** to **PDI^{2-}** was monitored by stopped-flow (SFM-3, Bio-
446	Logic). The OD intensity was followed at 612 nm (i.e., characteristic band of **PDI^{2-}**). A 100 μM solution was
447	prepared by dissolving **PDI** (1 mg, 0.60 μmol) in 50 mM borate buffer, pH 8. Afterwards, 9 mL of a 100 μM
448	**PDI** solution were reduced with 15 μL of a 400 mM $Na_2S_2O_4$ solution (in borate buffer) under constant stirring
449	rate (1000 rpm). Immediately after oxidation, the freshly oxidized **PDI$_{mon}$** solution and 9 mL of a 40 mM
450	$Na_2S_2O_4$ solution were added into the syringes. Then, 80 μL of freshly oxidized **PDI$_{mon}$** solution and 80 μL
451	of $Na_2S_2O_4$ solution were quickly mixed. The reduction kinetics was followed for 90 min by doing data
452	intervals of one minute. The data recording frequency was 0.2 ms for the first 2 s and 10 ms for one minute.
453	The evolution of the time constant τ_1 was obtained from fitting the next expression I = A·exp(τ_1/t). The
454	evolution of time constant τ_2 was obtained from fitting the next expression y = $A_2+(A_1-A_2)/(1 + exp((t-t_0)/\tau_2))$.
455	*A* values are constants.
456	
457	**Supramolecular oscillations.** Oscillations were tracked with a Basler CCD camera and a diode-array
458	spectrophotometer (Analytikjena, Specord S600). **PDI$_{mon}$** (2.25 mL) solutions (i.e., 100, 75, 50 and 25 μM)
459	were measured under continuous influx of a 400 mM $Na_2S_2O_4$ solution at constant stirring rate (i.e., 1000
460	rpm) in a well-ventilated box (constant oxygen supply and light) for 12 hours. Different flow rates (from 0.45
461	to 0.9 μL/min) were studied in order to map the state space. Red, green and blue channels were recorded
462	at 10 frames per second using a home-built matlab interface. UV-Vis spectra were recorded from 400 to 900
463	nm in 2 seconds, spectra were taken every 10 seconds. Waste and buffer experiment were performed by
464	adding 250 μL of waste or buffer after defined times.
465	
466	**Near-IR light scattering experiments.** The scattering intensity measurements during oscillations were
467	performed by using a home-built setup (cf. Supplementary Figure 9). A 905 nm laser line was obtained from
468	a CW tunable Ti:Sapphire laser (Spectra-Physics, Model 3900S) pumped by a Millennia eV (Spectra-
469	Physics, 15W diode-pumped solid state laser). This wavelength was selected because none of the three
470	species (**PDI**, **PDI$^{·-}$** and **PDI^{2-}**) have absorption at 905 nm. The laser power was adjusted to be 300 mW. A
471	collimated laser beam (d = 6 mm) was irradiated through the sample solution that was placed on a magnetic
472	stirring plate. Scattered light was collected by a first lens (Thorlabs, f = 100 mm Plano-Convex lens) and
473	focused by a second lens (Thorlabs, f = 25 mm Plano-Convex lens) on the InGaAs photodiode detector
474	(Thorlabs, DET10N/M). The voltage output was recorded by a multichannel data logger (Pico Technology,
475	ADC-20). Scattered light was collected from an off-centered position to avoid the disturbance by a vortex
476	generated by a stirring bar inside solution.
477	
478	**Confocal measurements.** Confocal micrographs were taken by using Zeiss LSM 710 confocal microscope
479	system with 10 x magnification. The samples were excited by continuous-wave laser at 488 nm. The
480	emission was measured from 500 nm to 700 nm using a spectral detector. Measurements were performed
481	by taking 10 μL aliquots during oscillations. Measurements were performed on a 75 μM **PDI** solution.
482	
483	**Supramolecular traveling fronts.** 1.5 mL of a 100 μM **PDI$_{mon}$** solution was injected into a 3D printed chip
484	(50 x 25 mm). The chip was printed in VeroClear on a Stratasys Objet 30 printer and contains two glass
485	cover slips separated by 1 mm. Solutions can be injected from either side of the chip. In order to perform the
486	experiment, 30 μL of **PDI$_{assem}$** seeds or buffer (a freshly oxidized 100 μM **PDI$_{mon}$** solution aged for 1 hour)
487	were injected on one side of the chip. Images were acquired using a stereoscope (Nikon SMZ7457)
488	equipped with a CCD camera, frames were recorded every 10 seconds for ~1.5 hours, or using a ZEISS
489	LSM 710 confocal microscope, frames were recorded every 1 second for 30 min.
490	
491	**Density measurements.** The density of **PDI^{2-}**, **PDI$_{mon}$** and **PDI$_{assem}$** species was measured by using an
492	Anton Paar DMA 500 density meter. 6 mL of a 100 μM **PDI** borate buffer solution was reduced to **PDI^{2-}** by
493	adding 4 μL of a 400 mM $Na_2S_2O_4$ solution. The density of **PDI^{2-}** species was measured (2 mL /
494	measurement was used). The density was measured after oxidation back to **PDI$_{mon}$** species and when
495	**PDI$_{mon}$** was aged for 1h leading to **PDI$_{assem}$**. All measurements were repeated at least 4 times.
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