JOURNAL OF
Materials
CHEMISTRY

Synthesis and nonlinear optical properties of functionalised polydiacetylenes and their complexes with transition metals

M. A. Camacho,[a] Ajoy K. Kar,[a] W. Edward Lindsell,[b] Christopher Murray,[b] Peter N. Preston[b] and Brian S. Wherrett[a]

Departments of [a]Physics and [b]Chemistry, Heriot-Watt University, Riccarton, Edinburgh, UK EH14 4AS. E-mail: W.E.Lindsell@hw.ac.uk

Received 4th January 1999, Accepted 30th March 1999

New polydiacetylenes (PDAs) have been prepared in which a ligating 2,2′-bipyridyl substituent is incorporated in the side-chain, **3a–d**. The formation of complexes of these polymers, and of a related (diethylamino)alkyl substituted PDA **4**, with transition metals has been studied. Coordination polymers containing nickel(II) **5a,b**, copper(II) **5c,d**, ruthenium(II) **6** and molybdenum(0) **7a–c** have been formed and characterised spectroscopically by comparison with appropriate model coordination compounds, including species derived from corresponding monomeric 1,3-diynes **1**. The nonlinear optical properties of PDA **4** and the coordination polymers **5–7** in solution have been investigated by the *z*-scan procedure. Values for the nonlinear absorption coefficient, α_2, and the nonlinear refractive index, n_2, have been derived and these are discussed in relation to the structures of the PDAs.

Introduction

Polydiacetylenes [PDAs] (*cf.* **3**) can be prepared from diacetylenes (*cf.* **1**) in a solid state (topochemical) polymerisation by thermal treatment or by UV and γ-irradiation.[1] PDAs are highly coloured materials, often red, blue or black and usually insoluble but some, including those with urethane,[2] sulfonate[3] and ester[4] side-chains, are soluble in common organic solvents. The highly unsaturated conjugated backbone of PDAs imparts unusual physical properties, including relatively large third-order optical nonlinearity.[5] Another interesting feature is their property of chromism[6] which can be induced thermally and photochemically, or in solution by variation of the solvent to non-solvent ratio (solvatochromism). An intriguing feature of PDAs containing carboxylic acid groups (*e.g.* polymers derived from **1a**,**b**) is the effect of pH on the absorption spectra: such materials are yellow in alkaline solution but red in acid.[7] Polydiacetylenes with pyridyl-ester substituents have also been reported and show similar colour changes on protonation or complexation with some transition metals.[8] This type of dichroic behaviour is attributed to a change of effective conjugation length of the polymer backbone, accompanied in some cases by aggregation effects.[3,9]

It is clear that conformational effects in the side-chains of PDAs can have a pronounced influence on physical properties. As an extension of the work of Patel *et al.*[7] and ourselves[10] on the carboxylic acids, we have reported further examples of ionomeric PDA materials including those containing quaternary ammonium and phosphonium side-chains.[11] We are particularly interested in establishing whether significant differences in nonlinear optical behaviour can be induced by subtle modifications in side-chain structure. We now describe the preparation of new PDAs **3a–d** in which the side-chains contain a ligating bipyridyl substituent; we also describe the conversion of these, and a related PDA functionalised with tertiary amine groups **4**, into coordination complexes of nickel(II), copper(II), ruthenium(II) and molybdenum(0). An investigation of the optical nonlinearity of new PDAs through use of the *z*-scan technique is described.

Results and discussion

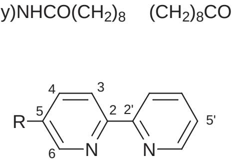
Syntheses

The previously reported[10] α,ω-dicarboxylic acids, $HO_2C(CH_2)_nC≡CC≡C(CH_2)_nCO_2H$, (**1a**, $n=3$; **1b**, $n=8$) and the monocarboxylic acid, $n\text{-}C_{10}H_{21}C≡CC≡C(CH_2)_8CO_2H$ **1c**, were treated with thionyl chloride in tetrahydrofuran (THF) to give the corresponding acid chlorides **1d–f**; the latter were not purified to analytical standard but were characterised by ^1H NMR spectroscopy. The corresponding amides **1g–i** were prepared routinely from the acid chlorides and 5-amino-2,2′-bipyridyl **2b**, although yields were only moderate. It was evident that the attempted transformation of **1e**⟶**1h** was incomplete since the methyl ester **1j** was also isolated from chromatographic purification using methanol as co-eluant, presumably from solvolysis of the intermediate α-amide ω-acid chloride.

$R^1—C≡C—C≡C—R^2$

1

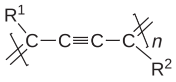
	R^1	R^2
a	$HO_2C(CH_2)_3$	$(CH_2)_3CO_2H$
b	$HO_2C(CH_2)_8$	$(CH_2)_8CO_2H$
c	$n\text{-}C_{10}H_{21}$	$(CH_2)_8CO_2H$
d	$ClOC(CH_2)_3$	$(CH_2)_3COCl$
e	$ClOC(CH_2)_8$	$(CH_2)_8COCl$
f	$n\text{-}C_{10}H_{21}$	$(CH_2)_8COCl$
g	5-(bipy)NHCO$(CH_2)_3$	$(CH_2)_3$CONH-5-bipy
h	5-(bipy)NHCO$(CH_2)_8$	$(CH_2)_8$CONH-5-bipy
i	$n\text{-}C_{10}H_{21}$	$(CH_2)_8$CONH-5-bipy
j	5-(bipy)NHCO$(CH_2)_8$	$(CH_2)_8CO_2Me$



2

	R
a	NO_2
b	NH_2

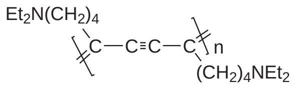
Successful polymerisation of diacetylenes **1g–j** was achieved by UV and/or γ-irradiation at room temperature, with unreacted monomer being subsequently removed by Soxhlet extraction with chloroform, followed by ethanol. Polymers **3a–d** varied from red **3d** to black **3b** in colour and were insoluble in common organic solvents, including dimethyl sulfoxide



3

	R¹	**R²**
a	5-(bipy)NHCO$(CH_2)_3$	$(CH_2)_3$CONH-5-bipy
b	5-(bipy)NHCO$(CH_2)_8$	$(CH_2)_8$CONH-5-bipy
c	5-(bipy)NHCO$(CH_2)_8$	$(CH_2)_8CO_2Me$
d	*n*-$C_{10}H_{21}$	$(CH_2)_8$CONH-5-bipy
e	*n*-$BuO_2CCH_2NHCO_2(CH_2)_4$	$(CH_2)_4O_2CNHCH_2CO_2Bu$-*n* (poly-4BCMU)

(DMSO) and *N*,*N*-dimethylformamide (DMF); investigation of their solid state structure by CPMAS $^{13}C\{^1H\}$ NMR spectroscopy confirmed the typical enyne backbone structure with resonances in the regions δ 100–107 (pink/red–black polymers) and *ca.* 130, corresponding to alkyne and alkene C-atoms, respectively.[12] The diethylamino-functionalised polydiacetylene **4** was prepared by reaction of the tosylated polydiacetylene, $[=C\{(CH_2)_4OTs\}-C\equiv C-C\{(CH_2)_4OTs\}]_n$ (PTS-12), with diethylamine, as reported earlier;[11] GPC analysis in THF of the PTS-12 employed in these reactions gave $\bar{M}_w = 1.5\times10^4$, $\bar{M}_w/\bar{M}_n = 2.7$ (in polystyrene equivalents).



4

Although PDA **4** is insoluble in water, stirring with aqueous solutions containing Ni^{2+} (from nickel(II) chloride) or Cu^{2+} (from copper(II) chloride), in varying molar ratios of metal ion : diethylamino groups, produced completely soluble materials with molar concentrations of $1–2\times10^{-2}$ M, based on the monomer unit. Materials with molar ratios $M^{2+}:NEt_2$ of 1 : 1, **5a**,**c**, and 1 : 2, **5b**,**d**, were specifically studied and it can be assumed that the metal ions become 6-coordinate in these species, containing coordination spheres of the type $[\{-NEt_2\}M(H_2O)_5]^{2+}$ and $[\{-NEt_2\}_2M(H_2O)_4]^{2+}$, respectively. In the latter species the two diethylamino groups may originate intramolecularly from the same PDA chain, or intermolecularly from separate PDA molecules leading to crosslinking; however, extensive crosslinking is probably not occurring as these metal-containing materials are appreciably water-soluble.

$$\text{polymer}(CH_2)_4NEt_2–M(H_2O)_5{}^{2+}\ 2\ Cl^-$$

5a M = Ni

5c M = Cu

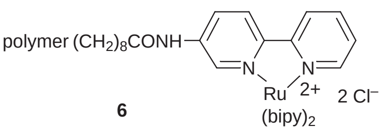
$$\left[\text{polymer}(CH_2)_4NEt_2\right]_2 M(H_2O)_4{}^{2+}\ 2\ Cl^-$$

5b M = Ni

5d M = Cu

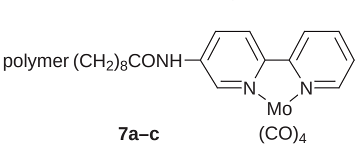
Solutions of the aminated-PDA **4** in chloroform showed a strong absorption band in the visible spectrum with λ_{max} < 500 nm, with a tail extending above 500 nm. On metallation this strong absorption was observed in aqueous solutions at λ_{max} ≈450 nm, and additional very weak, broad metal d–d bands were also present, as follows: Ni^{2+}-containing polymers, **5a**: λ_{max} ≈750 and ≈600 nm, **5b**: λ_{max} ≈615 nm; Cu^{2+}-containing polymers, **5c**: λ_{max} ≈740 nm, **5d**: λ_{max} between 620–650 nm. These metal-based bands are in the ranges reported for visible spectra of mono- and di-ammine or -amino complexes of nickel(II)[13,14] and copper(II),[13,15] respectively.

Reaction of the bipyridyl-functionalised polymer **3b** with *cis*-$Ru(bipy)_2Cl_2$[16,17] in refluxing methanol produced a soluble PDA containing polymer-[-bipyRu$(bipy)_2]^{2+}$ groupings, **6**;[16,18] the molar ratio of ruthenium(II) to polymer-bound bipyridyl groups in the reaction mixture and in the resulting soluble product was 1 : 1 and it may be assumed that most of these bipyridyl units had become coordinated to ruthenium, although the exact degree of metallation was not determined. A low molecular weight compound, $[CH_3(CH_2)_9C\equiv C–C\equiv C(CH_2)_8CONHbipyRu(bipy)_2]Cl_2$, was similarly formed by reaction of *cis*-$Ru(bipy)_2Cl_2$ with the diacetylene **1i** under the same conditions {*cf.* reported bis(diacetylene) derivative[8b]} and this showed the expected resonances, of correct relative intensities, in its ^1H NMR spectrum (see Experimental section). The absorption band of *cis*-$Ru(bipy)_2Cl_2$ with λ_{max} ≈550 nm was absent in the metallated PDA or diacetylene; the latter showed a metal to ligand charge transfer band, typical of tris(bipyridyl)ruthenium(II),[16] at λ_{max} 465 nm; in the polymeric derivative **6** this band was masked by the strong absorption of the conjugated enyne system which also extended above 500 nm giving a significant absorbance in the region 530–550 nm.



6

Thermal reaction of **3b** with molybdenum hexacarbonyl in DMF formed a soluble PDA, **7a**, containing -{bipy}$Mo(CO)_4$ terminal groups[19] on the side-chains. Similar reactions in DMF of $Mo(CO)_6$ with PDAs **3c**,**d** provided corresponding polymers **7b**,**c**, respectively, with a tetracarbonylmolybdenum fragment bound to the single bipyridyl group of each repeat unit. Although the extent of reaction in these polymeric systems was not specifically determined, the amounts of reactant employed should have caused metallation of all bipyridyl groups; spectroscopic comparisons with model compounds, and the absence of a band at 1980–2000 cm^{-1} in the IR spectra attributable to any unreacted $Mo(CO)_6$, supported complete conversion. Related tetracarbonylmolybdenum complexes of the monomeric diacetylenes **1h**,**i**,**j** were made by reactions with $Mo(CO)_6$ in refluxing toluene. The IR spectra of these model species showed four characteristic[19,20] ν(CO) bands in their IR spectra in the ranges 2016–2017, 1906–1909, 1877–1879, and 1829–1830 cm^{-1} (in toluene), of similar intensity and wavenumber to those of the polymeric analogues which show bands at 2011–2015, 1900–1907, 1875–1876, and 1829–1833 cm^{-1} (in DMF). The visible absorption due to the chromophore, $Mo(CO)_4$(bipy), is a metal-to-ligand charge transfer band in the region 440–500 nm,[21] which is masked by the intense polymer absorption of the PDAs.

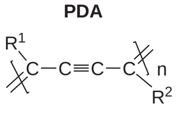


7a–c

Optical studies

The nonlinear optical properties of the new PDAs in solutions of suitable solvents were studied by the *z*-scan technique using open and closed aperture settings. All experiments were conducted at 532 nm, with the picosecond laser pulse-energies set lower than the corresponding damage energy and to avoid heating of the sample (<1.7 mJ $pulse^{-1}$). The absorption edges of the samples varied from less than 500 nm through to

Table 1 Nonlinear absorption coefficients (α_2), nonlinear refractive indices (n_2) and derived figures-of-merit T and W for PDA solutions from z-scan measurements at 532 nm

PDA 	Solvent	Conc.[a]	$\alpha_0{}^b$/cm^{-1}	α_2/cm GW^{-1}	n_2/10^{-15} cm^2 W^{-1}	T^c	W^c
$R^1=R^2=(CH_2)_4O_2CNHCH_2CO_2Bu^n$ (**3e**) (poly-4BCMU)	$CHCl_3$	0.014	4.8	1.4	−200	0.4	1.6
$R^1=R^2=(CH_2)_4NEt_2$ (**4**)	$CHCl_3$	0.0158	2	1.7	−62	1.5	3.0
$R^1=R^2=(CH_2)_4NEt_2+Ni(II)^d$ (**5a**)	H_2O	0.0165	1.8	1.6	−80	1.1	3.8
$R^1=R^2=(CH_2)_4NEt_2+Ni(II)^e$ (**5b**)	H_2O	0.0148	0.7	1.1	−50	1.2	6.2
$R^1=R^2=(CH_2)_4NEt_2+Cu(II)^d$ (**5c**)	H_2O	0.0192	2.3	1.8	−63	1.5	2.6
$R^1=R^2=(CH_2)_4NEt_2+Cu(II)^e$ (**5d**)	H_2O	0.0105	0.8	1.2	−53	1.2	6.4
$R^1=R^2=(CH_2)_8CONHbipyRu(bipy)_2{}^{2+}$ (**6**)	MeOH	0.0125	25.8	−6.5	−59		0.08
$R^1=R^2=(CH_2)_8CONHbipyMo(CO)_4$ (**7a**)	DMF	0.0069	1.1	0.47	28	0.9	2.4
$R^1=CH_3(CH_2)_9$ $R^2=(CH_2)_8CONHbipyMo(CO)_4$ (**7c**)	DMF	0.014	33.2	−8.5	61		0.06

[a] Molar concentration based on monomer unit. [b] Linear absorption coefficient. [c] Figures-of-merit, $T=\alpha_2\lambda/|n_2|$ and $W=|n_2|I/\alpha_0\lambda$. [d] Metal : nitrogen ratio = 1 : 1. [e] Metal : nitrogen ratio = 1 : 2.

550 nm. We were therefore probing a range of near-edge detunings with the 532 nm radiation. The linear absorption coefficients (α_0) for the typically 0.015 M concentration samples were around 1 cm^{-1} except for those metal–PDA complexes with bipyridyl ligands (Table 1). In sample **6** the presence of ruthenium leads to a broad absorption tail, extending beyond 532 nm, and in the molybdenum sample **7c** an absorption peak is actually on the long wavelength side of the laser wavelength.

Good fits to the z-scan results were achieved using the Huygens–Fresnel formalism,[22] accounting for the third-order nonlinearity, characterised by a nonlinear refractive index, n_2, and a nonlinear absorption, α_2. Fig. 1 and 2 depict examples of experimental data from the z-scans, and their theoretical fits. Values of the nonlinear coefficients deduced from these fits, and those for the other samples, are listed in Table 1. The closed aperture z-scans for the diethylamino-functionalised polymer **4** and its complexes with Ni^{2+} and Cu^{2+}, **5a–d**, indicate a negative n_2, characterised by a pre-focal (negative z-value) transmittance maximum followed by a post-focal (positive z-value) transmittance minimum. The nonlinear absorption coefficients for these PDAs are positive, corresponding to two-photon or induced absorption, characterised by a dip (centred at $z=0$) in the open-aperture z-scan traces. Parameters obtained under similar experimental conditions for a solution of the urethane-substituted PDA (poly-4BCMU) **3e**[2] in chloroform are included in Table 1. The nonlinear refractive indices correspond to third-order susceptibility [Re$\chi^{(3)}$] values for these dilute solutions of around 10^{-11} esu.

Fig. 3(a) presents the nonlinear results in such a way as to highlight trends. Assuming a linear dependence on concen-

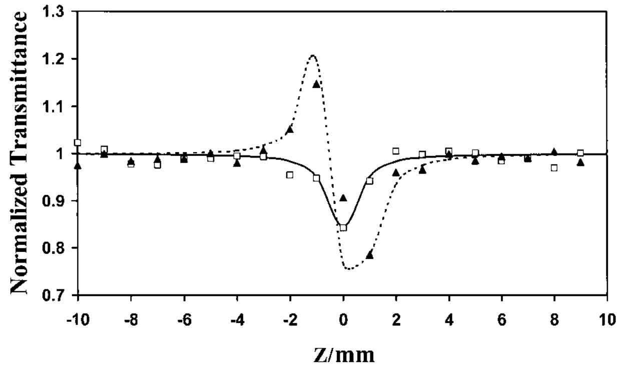


Fig. 1 z-Scan results for PDA **5b**: squares represent open aperture experimental results; triangles represent closed-aperture experimental results; full and dotted lines are the corresponding theoretical fits.

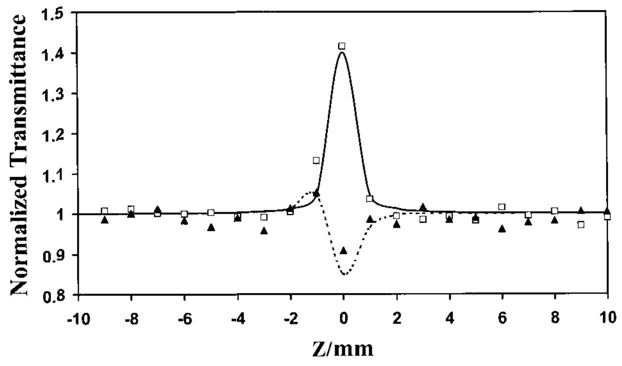


Fig. 2 z-Scan results for PDA **6**: squares represent open aperture experimental results; triangles represent closed-aperture experimental results; full and dotted lines are the corresponding theoretical fits.

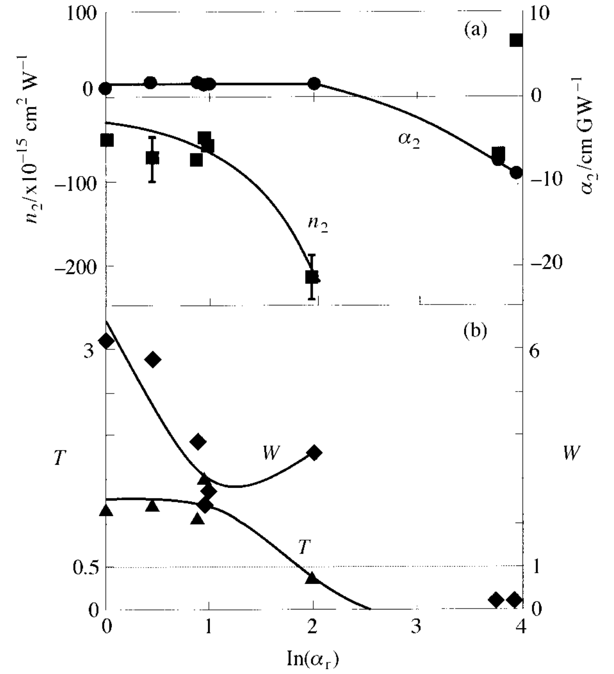


Fig. 3 (a) Optical nonlinearities, n_2 (squares) and α_2 (circles), (b) figures-of-merit W (diamonds) and T (triangles), for the PDA samples of Table 1. Nonlinearities are normalised for a concentration of 0.015 M; the relative absorption, α_r, is the absorption coefficient (at 0.015 M) relative to that of sample **5b**. From left to right the experimental points refer to samples in the order **5b**, **5d**, **4**, **5c**, **5a**, **6**, **7c**. The lines are guides to the eye.

tration, the coefficients are normalised to a 0.015 M concentration and plotted against the normalised linear absorption (on a log scale for clarity). The figure shows that for samples **3–5d** the induced absorption is essentially identical, whereas the nonlinear refraction increases as the absorption edge is approached. For the PDAs functionalised at the end of octamethylene side-chains with bipyridyl-metal complexes, for which the excitation wavelength is on or close to the absorption peak, saturation dominates, as is the case in solid PDA films.[23] At wavelengths longer than the peak wavelength this saturation leads to a negative refractive nonlinearity, sample **6**; for the molybdenum sample **7c** saturation of the peak at 550 nm is responsible for the observed positive n_2.

Fig. 3(a) demonstrates that the proximity to absorption peaks, which varies with the metallation, dominates the nonlinearity. It should also be noted that slightly different values of n_2 and α_2 have been measured for solutions of related Ni(II) and Cu(II) polymers, as reported in a preliminary communication,[24] but these PDAs had a substantially higher molar mass, being prepared from PTS-12 with $\bar{M}_w = 5.8 \times 10^5$ with a very wide polymodal mass distribution, including components around $M \approx 10^3$.

Several figures-of-merit (FOM) have been devised[25] in order to assess the usefulness of a nonlinear material for optical switching operations. If I_m is the maximum laser irradiance usable either before damage or before saturation of the nonlinearity itself, then the maximum achievable refractive index change, n_2I_m, must produce at least a π-phase change within the absorption length, which has a linear value of α_0^{-1}. The relevant FOM, at operating wavelength λ, is $W = |n_2|I_m/\alpha_0\lambda$. Almost regardless of the device configuration, for switching to be possible one requires $W > 1$. The absorption length itself will decrease, to $(\alpha_2 I)^{-1}$ if there is strong induced absorption. Hence a second FOM has been introduced, $T = \lambda\alpha_2/|n_2|$, with $T < 3$ required for switching in a nonlinear Fabry–Perot Etalon and $T < 0.5$ for a nonlinear directional-coupler. The T-criteria are not relevant for cases of saturating absorption (bleaching). Fig. 3(b) shows the trends in W and T for the PDA solutions; a value of $I = 5$ GW cm^{-2} was used in the evaluation of W. The values of W meet the criterion $W > 1$, except for samples **6** and **7c**, for which the high linear absorption prevents switching, and indeed for which heating occurred at peak irradiances exceeding 2 GW cm^{-2}. The T values are sufficient for Fabry–Perot, but not directional-coupler, switching except for the near resonance, 4BCMU, case. It should also be noted that these PDAs show fast (picosecond) nonlinear responses.[24]

Conclusions

PDAs can be prepared in which ligating groups (diethylamino and bipyridyl) are incorporated into the side-chains. New polymeric derivatives can be generated by subsequent treatment of these polymers with nickel(II), copper(II), ruthenium(II) and molybdenum(O) species. Evaluation of the nonlinear properties of the new materials using *z*-scan techniques demonstrates that the proximity of the radiation wavelength to the main absorption feature is the dominant influence on the strength of the refractive nonlinearity, which is the key parameter for optical switches. The ideal condition is confirmed as being close to the so-called $\mathrm{Im}\chi^{(3)} = 0$ point, where the nonlinear absorption disappears (*i.e.* $\alpha_2 = 0$). At wavelengths longer than the ideal, induced absorption can inhibit switching; at shorter wavelengths the strong linear absorption prevents switching. The ideal point occurs close to 532 nm in 4BCMU. In metallated diethylamino PDAs, **5b**,**d**, the blue-shift of the absorption feature with respect to the non-metallated amine implies optimum switching conditions at around 500 nm. In the PDAs with bipyridyl ligating groups the switching operation should be achievable at wavelengths longer than 550 nm.

Experimental

Organometallic reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Solvents used were dried under reflux and freshly distilled under a dry nitrogen atmosphere before use. Drying agents were: Na–benzophenone {for petroleum ether (bp 60–80 °C), diethyl ether, tetrahydrofuran (THF), and toluene}; and P_2O_5 (for dichloromethane). Infrared (IR) spectra were recorded on Perkin Elmer 580 and 1600 instruments and calibrated against polystyrene. ^{1}H and ^{13}C NMR spectra in solution were recorded at 200.13 and 50.32 MHz, respectively, on a Bruker WP 200 SY spectrometer; chemical shifts (ppm) are reported relative to tetramethylsilane as reference and coupling constants are quoted in Hz. Solid state CPMAS ^{13}C{^{1}H} NMR spectra (75.43 MHz) were recorded at the University of Durham, UK. UV/visible spectra were recorded on a Shimadzu UV-240 spectrophotometer. ^{60}Co γ-Irradiations were carried out at the SURRC, East Kilbride, Scotland, GPC analyses were by RAPRA Technology Ltd., Shrewsbury, UK, and elemental analyses were performed at UMIST, Manchester, UK, and at Heriot-Watt University. 10,12-Tricosadiynoic acid **1c** was purchased from Lancaster Synthesis Ltd., and used without further purification.

General procedure for the preparation of carboxylic acid chlorides, 1d–f

Thionyl chloride (*ca.* 2–4 molar excess) and the appropriate carboxylic acid **1a**,**b**,[10,26] **1c** and tetrahydrofuran (*ca.* 20–50 ml g^{-1} of carboxylic acid) were heated under reflux until the evolution of hydrogen chloride ceased. Excess thionyl chloride and solvent were evaporated under reduced pressure and the residual crude oily acid chlorides were used without further purification. The following were prepared:

5,7-Dodecadiyne-1,12-dicarbonyl chloride, 1d. ^{1}H NMR ($CDCl_3$) δ: 1.8 (m, 4H, CH_2), 2.21 (t, 4H, $J = 6.7$, $CH_2C{\equiv}C$), 2.9 (t, 4H, CH_2COCl).

10,12-Docosadiyne-1,22-dicarbonyl chloride, 1e. ^{1}H NMR ($CDCl_3$) δ: 1.16–1.78 (m, 24H, CH_2), 2.24 (t, 4H, $J = 6.7$, $CH_2C{\equiv}C$), 2.88 (t, 4H, $J = 7.3$, CH_2COCl).

10,12-Tricosadiyne-1-carbonyl chloride, 1f. ^{1}H NMR ($CDCl_3$) δ: 0.85 (t, 3H, $J = 6.2$, CH_3), 1.2–1.55 (br s, 28H, CH_2), 2.21 (t, 4H, $J = 6.4$, $CH_2C{\equiv}C$), 2.85 (t, 2H, $J = 7.2$, CH_2COCl). ^{13}C{^{1}H} NMR ($CDCl_3$) δ: 14.0, 19.1, 22.6, 24.9, 28.3, 28.6, 28.7, 28.8, 29.0, 29.2, 29.4, 29.5, 31.8, 46.9, 65.1, 65.3, 77.4, 173.6. IR ($CDCl_3$) cm^{-1}: 1790 (CO str).

5-Amino-2,2′-bipyridyl, 2b. Hydrazine hydrate (0.25 g, 5.0 mmol) was added dropwise to 5-nitro-2,2′-bipyridyl[27] (0.50 g, 2.49 mmol), palladium on charcoal (10%, 50 mg) and ethanol (50 ml) and the mixture was heated under reflux for 15 h under an atmosphere of nitrogen. The hot solution was filtered through Celite and the Celite was then washed with hot ethanol (10 ml). The filtrate was evaporated to low volume under reduced pressure and conc. hydrochloric acid was added until all the salt of **2b** had precipitated. This solid was then dissolved in water (20 ml) and decolourising charcoal added (≈2% w/w). After stirring the mixture for *ca.* 45 min, the charcoal was removed by filtration through Celite. The filtrate was basified with saturated aq. sodium hydroxide and then sodium chloride was added in portions until the solution was saturated. The solution was extracted with chloroform (4 × 20 ml) and the extract was evaporated to leave 5-amino-

2,2′-bipyridyl **2b** as a colourless solid (0.335 g, 78%), mp 135–136 °C (lit.[28] 136 °C). The spectroscopic parameters (IR, ^{1}H NMR) of **2b** were in agreement with reported data.[28]

General procedure for preparation of amides, 1g–j

The appropriate acid chloride derivative (2.4 mmol) in tetrahydrofuran (10 ml) was added slowly to a solution of 5-amino-2,2′-bipyridyl (2.0 mmol) and triethylamine (2.0 mmol) in tetrahydrofuran (10 ml). After stirring at room temperature for 30 min, the resultant precipitate was washed with tetrahydrofuran (10 ml), then dichloromethane (20 ml) and was finally dried *in vacuo*. The product amides were then recrystallised from ethanol to give colourless solids that turned pink in daylight. The following were isolated:

Bis[*N*-5′(2′,2″-bipyridyl)]-5,7-dodecadiyne-1,12-diamide, 1g. mp 253–255 °C (decomp.) (32%). IR (KBr) cm^{-1}: 3303 (NH str), 1661 (C=O str), 1523 (NH def). Found: C, 72.5; H, 5.4; N, 15.5. $C_{32}H_{28}N_6O_2$ requires: C, 72.7; H, 5.3; N, 15.9%. ^{1}H NMR (d_6-DMSO) δ: 1.8 (m, 4H, CH_2) 2.21 (t, 4H, $J=6.5$, $CH_2C{\equiv}C$), 2.41 (m, 4H, $C\mathit{H}_2CONH$,), 7.39 (ddd, 2H, $J=7.4$, $J=3.7$, $J=1.1$, ArH), 7.9 (td, 2H, $J=7.7$, $J=1.8$, ArH) 8.19 (dd, 2H, $J=8.7$, $J=2.5$, ArH), 8.32 (dd, 4H, $J=8.7$, $J=4.9$, ArH), 8.63 (ddd, 4H, $J=4.7$, $J=1.5$, $J=0.8$, ArH), 8.82 (br d, 2H, $J=2.1$, ArH), 10.34 (br s, 2H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 18.4, 23.9, 35.4, 66.2, 78.1, 120.3, 121.0, 124.0, 127.1, 136.7, 137.6, 140.5, 149.6, 150.2, 155.5, 171.6. *m*/*z* (FAB): 529 $(M+H)^+$ (100%).

Bis[*N*-5′(2′,2″-bipyridyl)]-10,12-docosadiyne-1,22-diamide, 1h. This compound, and the ester **1j**, were isolated after chromatography of the crude product [silica gel, dichloromethane–methanol (95:5) eluant].

1h, mp 82–85 °C (decomp.) (39%). IR (KBr) cm^{-1}: 3279 (NH str), 2929, 2848 (CH str), 1660 (C=O str), 1532 (NH def). Found: C, 75.2; H, 7.4; N, 12.4. $C_{42}H_{48}N_6O_2$ requires: C, 75.4; H, 7.2; N, 12.6%. ^{1}H NMR (d_6-DMSO) δ: 1.3–1.4 (br s, 20H, CH_2), 1.6 (m, 4H, CH_2), 2.21 (t, $J=6.9$, 4H, $CH_2C{\equiv}C$), 2.40 (t, 4H, $J=7.4$, CH_2CONH), 7.40 (ddd, 2H, $J=7.5$, $J=4.9$, $J=1.1$, ArH), 7.91 (td, 2H, $J=7.6$, $J=1.8$, ArH), 8.21 (dd, 2H, $J=8.7$, $J=2.4$, ArH), 8.33 (dd, 4H, $J=8.8$ $J=4.7$, ArH), 8.65 (ddd, 2H, $J=4.6$, $J=1.6$, $J=0.8$, ArH), 8.83 (d, 2H, $J=1.9$, ArH), 10.29 (br s, 2H, NHCO).

1j, mp 83–85 °C (36%). $R_f=0.63$ (CH_2Cl_2–CH_3OH 9:1). Found: C, 74.5; H, 8.3; N, 7.8. $C_{33}H_{43}N_3O_3$ requires: C, 74.8; H, 8.2; N, 7.9%. ^{1}H NMR ($CDCl_3$) δ: 1.30–1.80 (br s, 24H, CH_2), 2.21 (m, 6H, $CH_2C{\equiv}C$ and $C\mathit{H}_2COOMe$), 2.40 (t, 2H, $J=7.3$, CH_2CONHR), 3.65 (s, 3H, $C\mathit{H}_3OCOR$), 7.27 (ddd, 1H, $J=7.4$, $J=4.8$, $J=1.2$, ArH), 7.50 (br s, 1H, NHCO), 7.80 (dt, 1H, $J=7.8$, $J=1.8$, ArH), 8.26 (dd, 1H, $J=8.6$, $J=2.4$, ArH), 8.37 (dd, 2H, $J=8.6$, $J=2.5$, ArH), 8.65 (ddd, 2H, $J=4.8$, $J=1.8$, $J=0.8$, ArH). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 19.1, 24.8, 25.3, 28.2, 28.6, 28.7, 28.8, 29.0, 29.1, 34.0, 37.5, 51.4, 65.2, 77.6, 120.6, 121.2, 123.3, 127.4, 135.0, 136.8, 140.1, 151.5, 171.8, 174.3. *m*/*z* (EI): 529 M^+ (21%).

[*N*-5′(2′,2″-bipyridyl)]-10,12-tricosadiyne-1-amide, 1i. mp 95–96 °C (39%). $R_f=0.4$ (CH_2Cl_2–CH_3OH 9:1). Found: C, 78.9; H, 9.2; N, 8.2. $C_{33}H_{45}N_3O$ requires: C, 79.3; H, 9.1; N, 8.4%. ^{1}H NMR (d_6-DMSO) δ: 0.88 (t, 3H, CH_3), 1.20 (br s, 26H, CH_2), 1.6 (m, 2H, CH_2), 2.21 (t, 4H, $J=6.3$, $CH_2C{\equiv}C$), 2.40 (t, 2H, $J=7.2$, CH_2CONH), 7.39 (ddd, 1H, $J=7.5$, $J=4.8$, $J=1.2$, ArH), 7.89 (td, 1H, $J=7.8$, $J=1.8$, ArH), 8.20 (dd, $J=8.7$, $J=2.5$, ArH), 8.32 (dd, 2H, $J=8.7$, $J=4.9$, ArH), 8.63 (ddd, 1H, $J=4.8$, $J=1.6$, $J=0.8$, ArH), 8.83 (d, 1H, $J=2.4$, ArH), 10.29 (br s, 1H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ: 14.0, 19.1, 22.6, 25.3, 28.2, 28.7, 28.8, 29.0, 29.2, 29.37, 29.44, 31.8, 33.1, 37.2, 65.2, 77.5, 120.8, 121.4, 123.4, 127.7, 135.8, 137.3, 140.1, 148.6, 150.1, 154.8, 172.6. *m*/*z* (FAB): 500.8 $(M+H)^+$ (15%).

General procedure for preparation of polydiacetylenes, 3a–d

Sample **1g** was suspended in water under a nitrogen atmosphere and irradiated with a 400 W medium pressure Hg lamp for 48 h at ambient temperature. Samples of monomer **1h**,**i** were sealed in evacuated Pyrex glass ampoules and subjected to γ-irradiation (20 Mrad, ambient temperature). The crude polymeric material obtained from either UV or γ-irradiation was purified by successive Soxhlet extractions with chloroform and then ethanol to remove unreacted monomer. The residual polydiacetylenes were dried *in vacuo* to yield polymers **3a–d**. All the polymers were very insoluble in common organic solvents, including dimethyl sulfoxide and *N*,*N*-dimethylformamide. The chloroform-soluble diethylamino-functionalised PDA **4** was prepared from PTS-12, as reported previously.[11]

Polydiacetylene, 3a, from monomer, 1g. CPMAS $^{13}C\{^1H\}$ NMR δ: 22.9, 34.8, 100.5, 121.9, 131.5, 136.4, 148.3, 152.0, 154.9, 172.6. IR (KBr) cm^{-1}: 3421, 3283, 2950, 1654, 1593, 1529, 1460, 1434.

Polydiacetylene, 3b, from monomer, 1h. Found: C, 74.0; H, 7.1; N, 12.2. $[C_{42}H_{48}N_6O_2]_n$ requires: C, 75.4; H, 7.2; N, 12.6%. CPMAS $^{13}C\{^1H\}$ NMR δ: 21.1, 26.1, 29.2, 33.4, 37.3, 106.5, 122.1, 129.9, 132.7, 142.4, 148.3, 152.0, 155.0, 172.4. IR (KBr) cm^{-1}: 3546, 3466, 3414, 3285, 2919, 2848, 1655, 1522, 1458.

Polydiacetylene, 3c, from monomer, 1j. Found: C, 73.4; H, 8.1; N, 7.2. $[C_{33}H_{43}N_3O_3]_n$ requires C, 74.8; H, 8.2; N, 7.9%. CPMAS $^{13}C\{^1H\}$ NMR δ: 26.8, 33.6, 37.1, 50.95, 101.4, 121.6, 129.9, 133.6, 136.7, 142.4, 149.0, 152.8, 155.0, 172.8. IR (KBr) cm^{-1}: 3474, 3416, 3284, 2919, 2848, 1734, 1654, 1522, 1458.

Polydiacetylene, 3d, from monomer, 1i. Found: C, 78.1; H, 9.2; N, 8.2. $[C_{33}H_{45}N_3O]_n$ requires: C, 79.3; H, 9.1; N, 8.4%. CPMAS $^{13}C\{^1H\}$ NMR δ: 14.7, 25.2, 33.6, 37.3, 101.1, 121.04 129.7, 171.4. IR (KBr) cm^{-1}: 3546, 3474, 3416, 3296, 2918, 2848, 1654, 1526, 1459.

Preparation of nickel and copper complexes 5a–d of diethylamino-substituted polydiacetylene, 4

The PDA **4** (0.050 g, 0.165 mmol monomer units) and nickel(II) chloride hexahydrate (0.78 g, 0.33 mmol) were added to water (10 ml) and the mixture stirred at ambient temperature for 24 h, after which a clear yellow–orange solution of **5a** was produced. A similar procedure was employed to form a polymer with 2:1 mol equiv. of $NEt_2:Ni^{2+}$ units **5b** and to form copper complexes of PDA containing 1:1 **5c** and 2:1 **5d** ratios of $NEt_2:Cu^{2+}$ units, using copper(II) chloride dihydrate. The following quantities of reagents were used: 1:1 $NEt_2:Ni^{2+}$ complex: PDA, 0.050 g; $NiCl_2{\cdot}6H_2O$, 0.078 g. 2:1 $NEt_2:Ni^{2+}$ complex: PDA, 0.045 g; $NiCl_2{\cdot}6H_2O$, 0.035 g. 1:1 $NEt_2:Cu^{2+}$ complex: PDA, 0.064 g; $CuCl_2{\cdot}2H_2O$, 0.072 g. 2:1 $NEt_2:Cu^{2+}$ complex: PDA 0.117 g; $CuCl_2{\cdot}2H_2O$ 0.066 g.

Reactions of bipyridyl-substituted polydiacetylenes and related diacetylenes with *cis*-Ru(bipy)$_2$Cl$_2$·2H$_2$O and Mo(CO)$_6$

(i) The polydiacetylene **3b** and *cis*-Ru(bipy)$_2$Cl$_2$·2H$_2$O[17] (2 mol equiv. for each repeat unit in **3b**) in dry, degassed methanol (*ca.* 10 ml) were heated under reflux for 48 h to form a completely soluble polymer, **6**, with -(bipy)Ru(bipy)$_2$Cl$_2$ terminated side chains. In a similar reaction, the diacetylene **1i** was allowed to react with one mol equiv. of *cis*-

$Ru(bipy)_2Cl_2{\cdot}2H_2O$ to form the ruthenium(II) species, $[CH_3(CH_2)_9C{\equiv}C{-}C{\equiv}C(CH_2)_8CONHbipyRu(bipy)_2]Cl_2$; ^1H NMR (D_2O) δ: 7.0–8.8 (*ca.* 23H, ArH), 1.9–2.4 (*ca.* 6H, CH_2CONH and $CH_2C{\equiv}C$) and 0.6–1.5 (*ca.* 31H, CH_3 and CH_2); λ_{max} (MeOH) 465 nm.

(ii) Polydiacetylenes **3b–d** (1 mol equiv.) and molybdenum hexacarbonyl [Aldrich; 2 mol equiv. with respect to each repeat unit in **3b**, or 1 mol equiv. for each repeat unit in **3c** or **3d**, respectively] were heated in dry, degassed *N*,*N*-dimethylformamide (DMF, 200 ml g^{-1} PDA) at 100 °C for 48 h to form solutions of polymers with -(bipy)$Mo(CO)_4$ terminated side-chains, **7a**, **7b** and **7c**, respectively. Related reactions of the diacetylenes **1h–j** with $Mo(CO)_6$ in toluene under reflux for 16 h produced the corresponding tetracarbonylmolybdenum derivatives of the monomers.

Spectral properties of the above solutions of metal-containing polymers and of the low molecular weight model compounds are described in the Results and discussion section.

Optical measurements

z-Scan experiments were carried out on 1 mm thick solutions of a PDA at known concentration in a suitable solvent, as listed in Table 1. The laser system used in this work was a Coherent Antares Nd:YAG laser modelocked at 76 MHz by an acoustic optic modulator. The Antares provided 1.06 μm 532 nm outputs. The visible output was used to synchronously pump a dual-jet Coherent 702 dye laser. The tuneable dye laser was amplified *via* a Continuum Regenerative Amplifier (RGA) and a 3-stage Continuum Pulse Tuneable dye Amplifier (PTA). The regenerative amplifier could be run at 2, 5 or 10 Hz. Output pulses of approximately 0.7 ps duration (full-width at half-maximum) and up to 1 mJ $pulse^{-1}$ were obtainable, both parameters depending on the particular combination of laser dyes being used. The output was attenuated to <1.7 μJ $pulse^{-1}$ for measurements on PDAs to avoid sample damage.

To evaluate the nonlinear refractivity, a standard *z*-scan set-up was used. A Gaussian beam, which is critical for the *z*-scan measurement, was extracted by a spatial filter using a diamond pin-hole (100 μm) in an evacuated chamber. The detection system was calibrated using a Laser Precision Rj-7200 pyro-electric energy meter. Transmittance of a sample with and without a finite aperture in the far field was measured as the sample was scanned through the focal plane along the propagation direction *z*. At each position, 40 laser shots were averaged in order to reduce noise. The movement of the sample was achieved using a translation stage: the transmitted and reference energies were measured using three silicon photodiode detectors. The system was automatically controlled by a computer program with which it was possible to monitor the sample position and the readings of each detector simultaneously. This enabled both open- and closed-aperture signals to be recorded at the same time. The nonlinear refractive index (n_2) and the nonlinear absorption coefficient (α_2) were calculated from the *z*-scan signals using the procedure developed by Sheik-Bahae *et al.*[29]

Acknowledgements

We thank the EPSRC and Heriot-Watt University for funding and Dr D. C. Apperley for provision of CPMAS NMR spectra through the EPSRC service at the University of Durham, UK. M. A. Camacho thanks Conacyt-Mexico for a scholarship.

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