Supplementary Material (ESI) for Chemical Communications

Supplementary Information

"On-demand" control of thermoresponsive properties of poly(*N*-isopropylacrylamide) with cucurbit[8]uril host-guest complexes

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1 Experimental

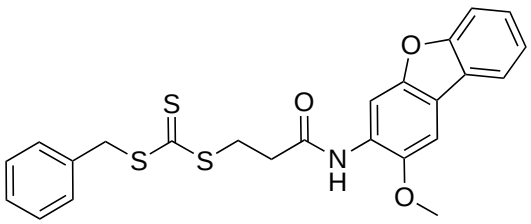
1.1 Materials

All starting materials were purchased from Alfa Aesar or Sigma Aldrich and were used as received unless stated otherwise. 2,2'-azobisisobutyronitrile (AIBN) was recrystallized twice from methanol. *N*-isopropylacrylamide (NIPAM) was recrystallized twice from hexane. 3-Benzylsulfanylthiocarbonylsulfanyl propionic acid and cucurbit[8]uril (CB[8]) were prepared according to literature procedures.[1,2]

1.2 Characterization techniques

^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 500 BB-ATM and Bruker Avance 500 TCI (both 500 MHz) spectrometers. UV/visible spectroscopy was performed on a Varian Cary Bio 100 UV-Vis spectrophotometer with temperature controller. Gel permeation chromatography (GPC) analysis was carried out using water as the eluent. The aqueous GPC setup consisted of a Shodex OHpak SB column, connected in series with a Shimadzu SPD-M20A prominence diode array detector, a Wyatt DAWN HELEOS multi-angle light scattering detector and a Wyatt Optilab rEX refractive index detector.

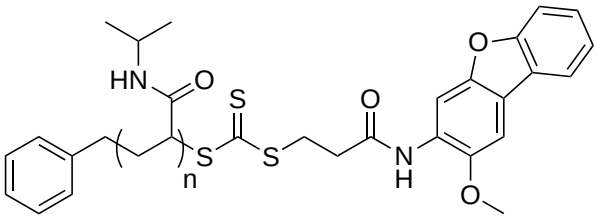
1.3 Synthesis of CTA1



Chain transfer agent **CTA1** was synthesised by an amidation reaction between 3-benzylsulfanylthiocarbonylsulfanyl propionic acid and 3-amino-2-methoxy dibenzofuran (see Scheme 1).[3] A 50 mL RB flask was charged with 3-benzylsulfanylthiocarbonylsulfanyl propionic acid (0.54 g, 2 mmol), N,N'-dicyclohexylcarbodiimide (1.03 g, 5 mmol), 3-amino-2-methoxy-dibenzofuran (0.36 g, 1.67 mmol) and dry dichloromethane (25 mL). The reaction mixture

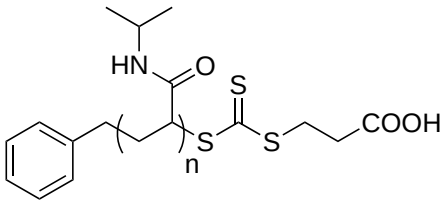
was then stirred at room temperature overnight. A white precipitate formed was filtered off and discarded. The solvent was removed under reduced pressure and the product was then isolated by column chromatography (silica gel, 95:5 chloroform/hexane) as a yellow powder (0.27 g, 29%). ^{1}H NMR ($CDCl_3$): δ = 8.75 (s, 1H), 8.11 (s, 1H), 7.88 (d, 1H), 7.57 (d, 1H), 7.4-7.3 (m, 8H), 4.66 (s, 2H), 4.05 (s, 3H), 3.82 (t, 2H), 2.93 (t, 2H) ppm; ^{13}C NMR ($CDCl_3$): δ = 223.7, 168.4, 156.7, 150.8, 144.6, 134.8, 129.3, 128.7, 127.8, 126.3, 124.5, 122.5, 119.8, 118.5, 111.7, 103.5, 101.0, 56.4, 41.5, 36.5, 31.9 ppm. Anal. Calcd for $C_{24}H_{21}NO_3S_3$: C, 61.64; H, 4.53; N, 3.00. Found: C, 61.42; H, 4.48; N, 3.16.

1.4 Synthesis of P1



Monofunctional poly(*N*-isopropylacrylamide) terminated by a dibenzofuran (DBF) end group, **P1**, was synthesised *via* reversible addition-fragmentation chain transfer (RAFT) polymerisation using **CTA1**. A dry vial was charged with chain transfer agent **CTA1** (37.4 mg, 0.08 mmol), NIPAM (0.40 g, 3.53 mmol), AIBN (1.3 mg, 0.008 mmol), 1,4-dioxane (1.8 mL) and a stir bar. The solution was degassed thoroughly using three freeze-pump-thaw cycles, back-filled with nitrogen and then stirred in an oil bath preheated to 70 ^{o}C. After 7 h the polymerization mixture was quenched in liquid nitrogen and **P1** was isolated by precipitating the mixture twice into cold diethyl ether. M_n^{NMR} (g/mol) = 5000, M_n^{GPC} (g/mol) = 7100, PDI = 1.08. ^{1}H NMR ($CDCl_3$): δ = 8.72 (s, 1H), 8.13 (s, 1H), 7.88 (d, 1H), 7.58 (d, 1H), 7.40-7.09 (m, 8H), 6.43 (broad, n*1H), 4.04 (s, 3H), 4.02 (s, n*1H), 3.82 (broad, 2H), 2.90 (broad, 2H), 2.32-1.50 (broad, n*3H), 1.16 (broad, n*6H) ppm.

1.5 Synthesis of P2



Control PNIPAM **P2** was synthesised *via* RAFT polymerisation using the unmodified CTA 3-benzylsulfanylthiocarbonylsulfanyl propionic acid. A dry vial was charged with CTA (46.31 mg, 0.17 mmol), NIPAM (0.85 g, 7.51 mmol), AIBN (2.87 mg, 0.017 mmol), 1,4-dioxane (3.8 mL) and a stir bar. The solution was degassed thoroughly using three freeze-pump-thaw cycles, back-filled with nitrogen and then stirred in an oil bath preheated to 70 ^{o}C. After 18 h the polymerization mixture was quenched in liquid nitrogen and **P2** was isolated by precipitating the mixture into cold ether. M_n^{NMR} (g/mol) = 5100, M_n^{GPC} (g/mol) = 6500, PDI = 1.06. ^{1}H NMR ($CDCl_3$): δ = 7.20-7.06 (m, 5H), 6.40 (broad, n*1H), 4.05 (s, n*1H), 3.00-2.95 (broad, 2H), 2.85 (broad, 2H), 2.33-1.48 (broad, n*3H), 1.14 (broad, n*6H) ppm.

2 Supporting Figures S1-S6

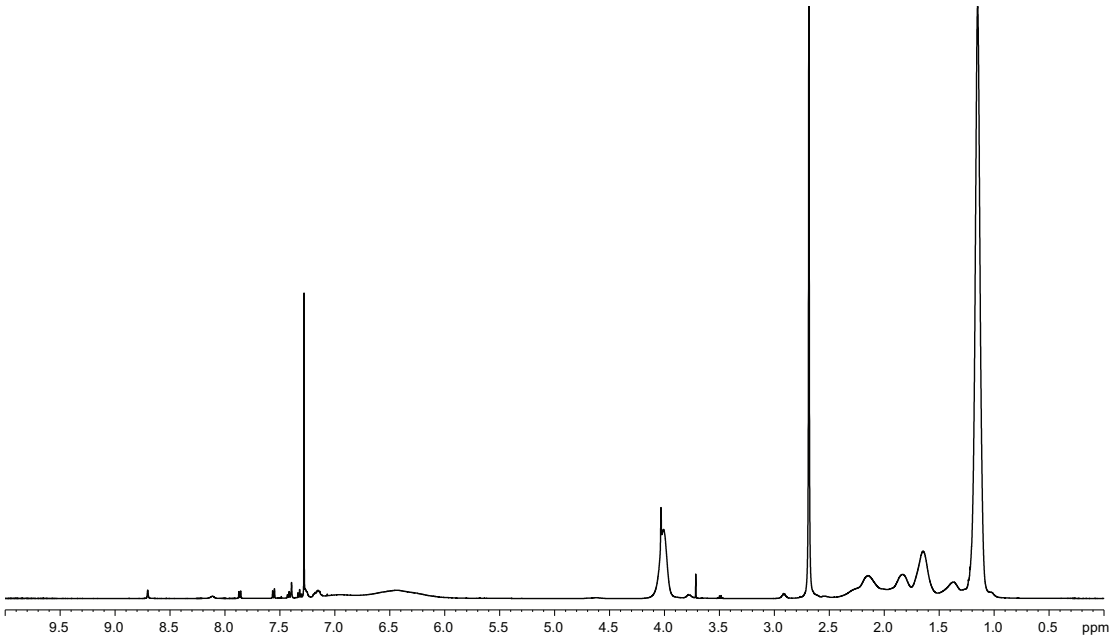


Figure S1: ^{1}H NMR (500 MHz, $CDCl_3$) of **P1**.

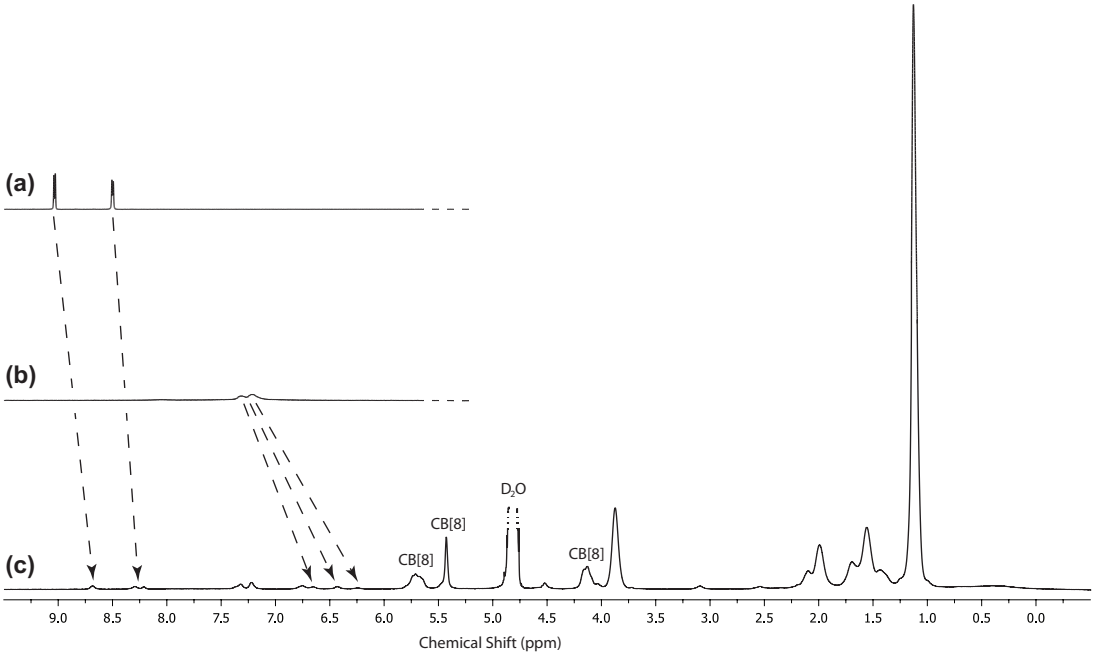


Figure S2: Partial ^{1}H NMR spectra (500 MHz, D_2O) at 20 ^oC of $\mathbf{M_2V}$ (a) and **P1** (b), and full ^{1}H NMR spectrum (500 MHz, D_2O) at 20 ^oC of **P1**+$\mathbf{M_2V}\subset$**CB[8]** (c). The signals corresponding to the resonance of the solvent protons have been truncated for clarity.

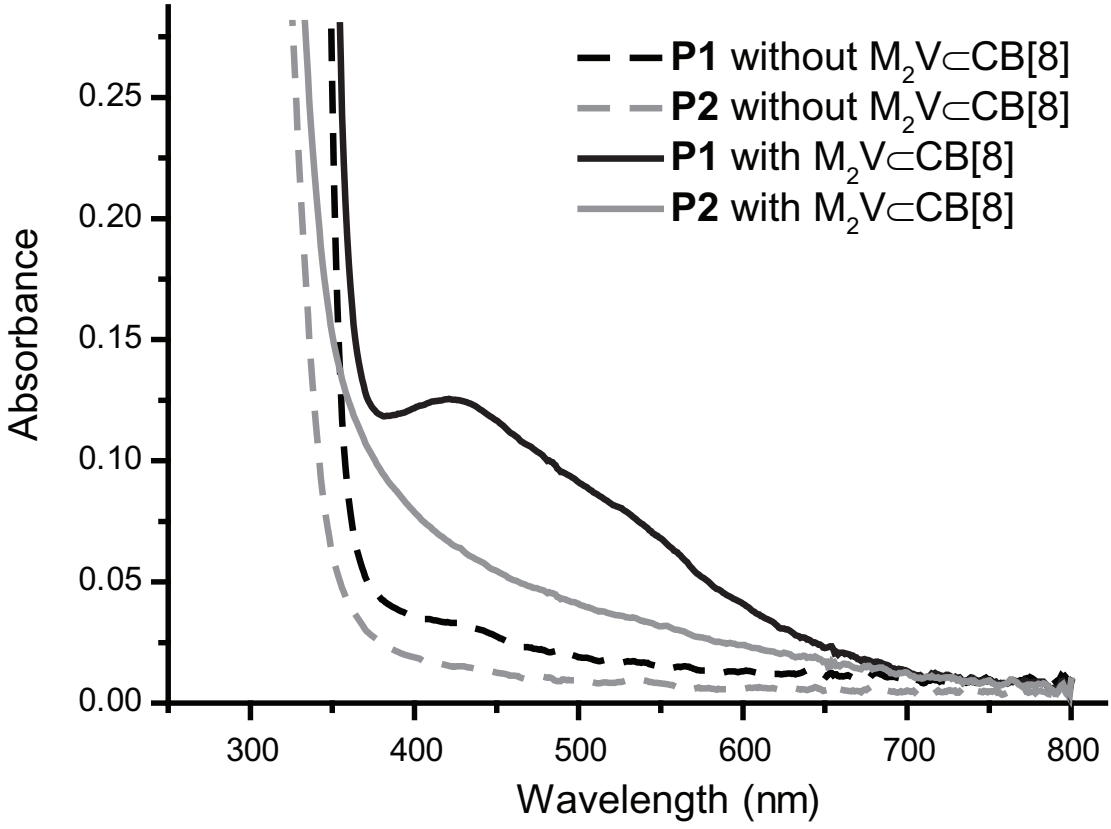


Figure S3: UV/vis spectra of aqueous solutions of **P1** (dotted black line), **P2** (dotted grey line), **P1** in the presence of 1 equiv of $\mathbf{M_2V}\subset\mathbf{CB[8]}$ (solid black line) and **P2** in the presence of 1 equiv of $\mathbf{M_2V}\subset\mathbf{CB[8]}$ (solid grey line).

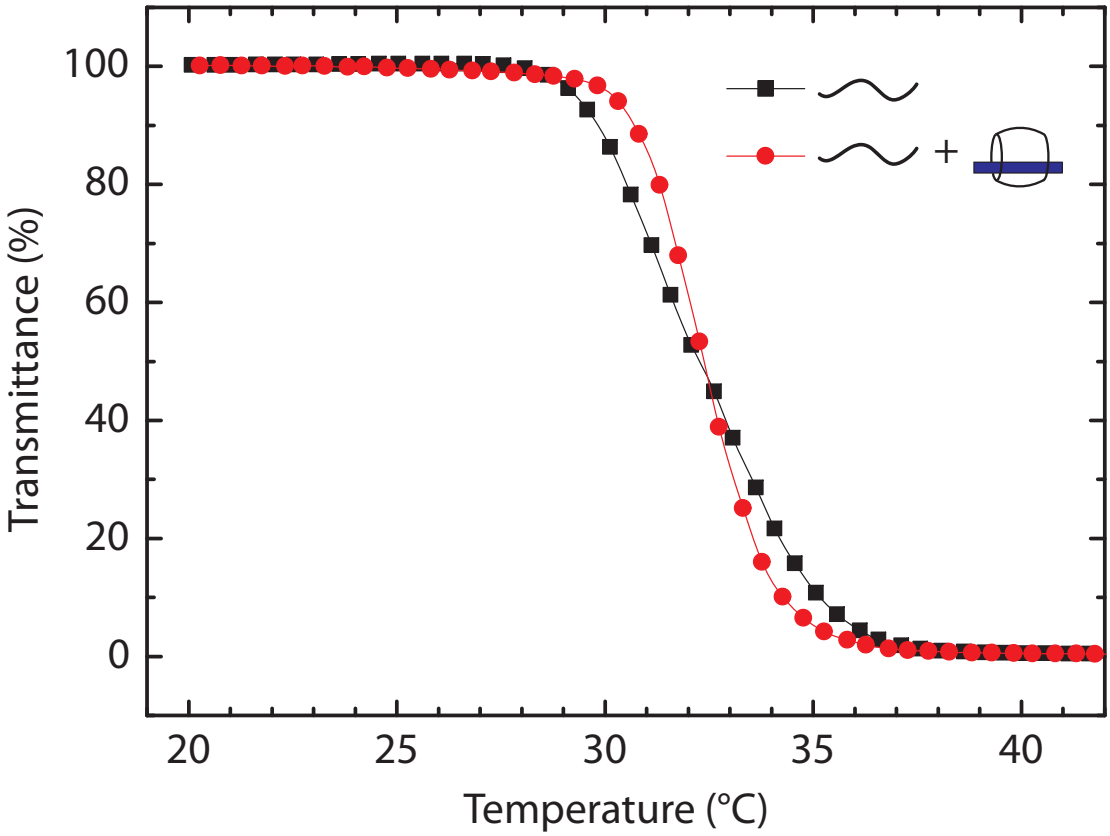


Figure S4: Thermosensitive phase transition plots of **P2** (0.2 mM in water) in the absence (black squares) and presence (red circles) of $\mathbf{M_2V}\subset\mathbf{CB[8]}$. Recorded at 600 nm and at a heating rate of 1 ^{O}C/min.

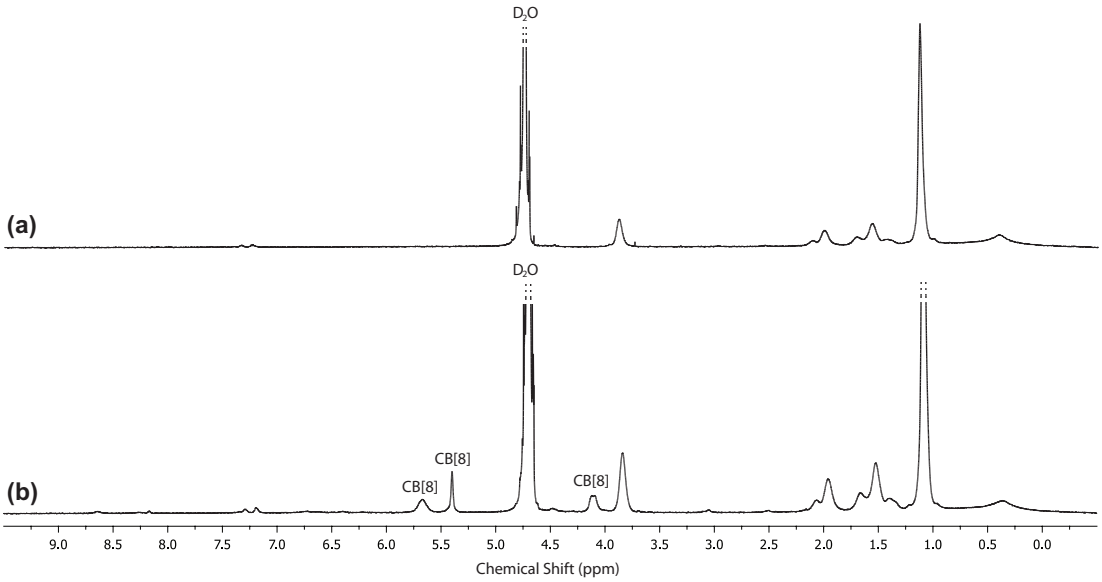


Figure S 5: ^{1}H NMR spectra (500 MHz, D_2O) at 26 ^{o}C of (a) **P1** (0.25 mM) and (b) **P1**+$\mathbf{M_2V}\subset$**CB[8]** (0.25 mM). To prepare (b), 0.5 mL of a solution containing $\mathbf{M_2V}\subset$**CB[8]** (0.5 mM) and **P1** (0.25 mM) in D_2O and equilibrated at 26 ^{o}C was added to 0.5 mL of the sample in (a), and its spectrum recorded immediately.

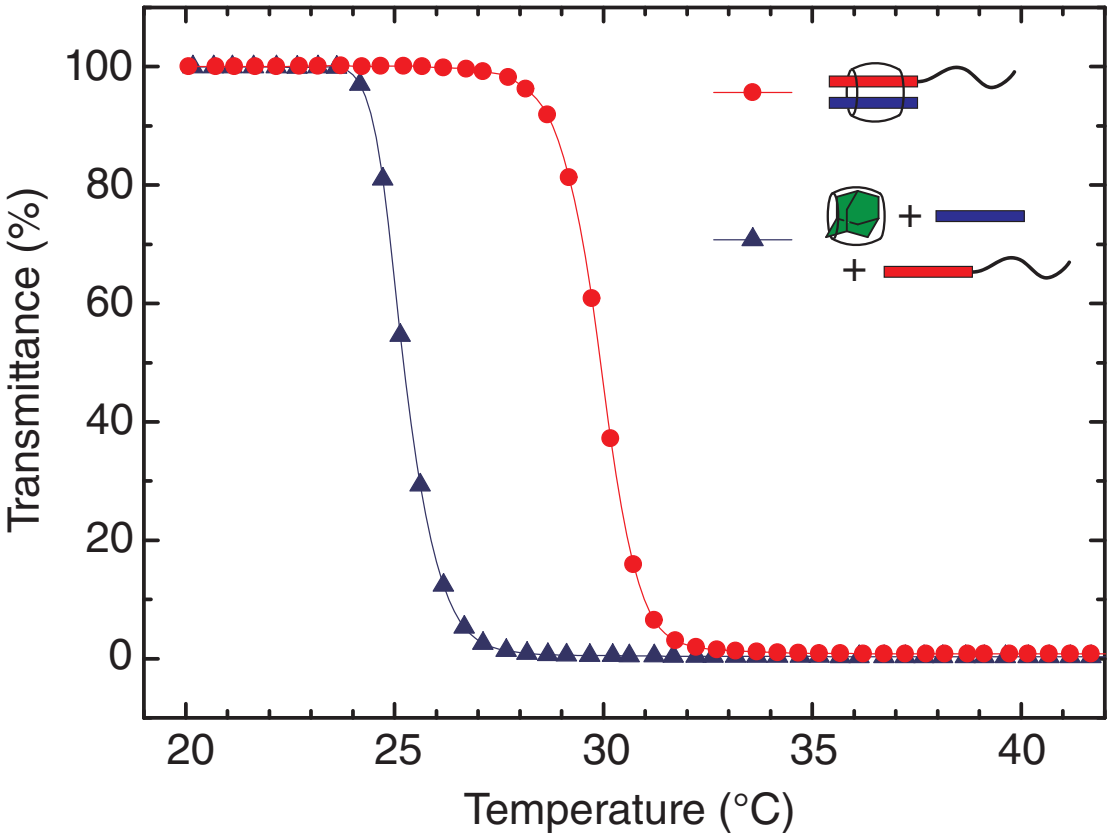


Figure S6: Thermosensitive phase transition plot of **P1**+$\mathbf{M_2V}$⊂**CB[8]** (0.2 mM in water) in the absence (red circles) and presence (blue triangles) of 1-aminoadamantane. Recorded at 600 nm and at a heating rate of 1 ^{o}C/min.

References

[1] Skey, J. & O'Reilly, R. K. Facile one pot synthesis of a range of reversible addition-fragmentation chain transfer (RAFT) agents. *Chem. Commun.* 4183–4185 (2008).

[2] Huang, W.-H., Liu, S. & Isaacs, L. Cucurbit[n]urils. In Diederich, F., Stang, P. & Tykwinski, R. R. (eds.) *Modern Supramolecular Chemistry, Strategies for Macrocycle Synthesis* (Wiley-VCH, Weinheim, 2008), 1 edn.

[3] Zayed, J. M., Biedermann, F., Rauwald, U. & Scherman, O. A. Probing cucurbit[8]uril-mediated supramolecular block copolymer assembly in water using diffusion NMR. *Polymer Chemistry* **1**, 1434–1436 (2010).