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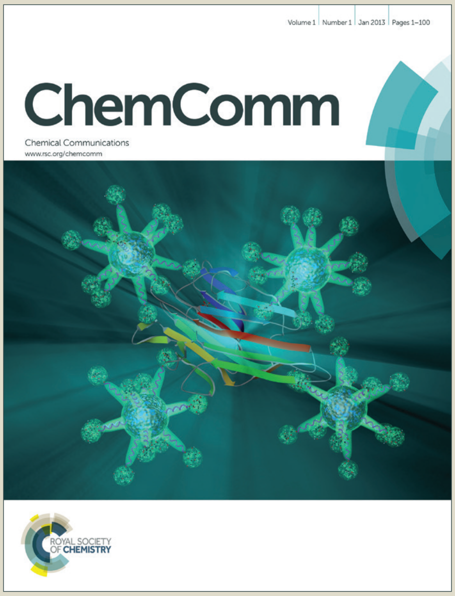

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Cite this: DOI: 10.1039/x0xx00000x

Photochromism in Sound-induced Alignment of a Diarylethene Supramolecular Nanofibre

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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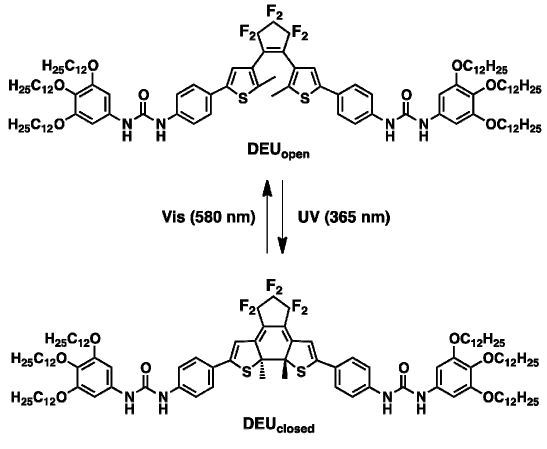
A photochromic supramolecular nanofibre, composed of a diarylethene derivative, exhibits hydrodynamic alignment under exposure to the audible sound. The aligned nanofibre outputs linear dichroism (LD), whose wavelength region can be switched reversibly with UV and visible light.

Intelligent materials adapt their functions in response to external stimuli and environmental changes.[1] Sonoresponsive molecules or molecular assemblies, whose sample solutions induce dichroism and/or birefringence when exposed to sound, are an example.[2–7] Some nanoscale objects such as polymers and colloidal particles in solutions are known to align under exposure to an ultrasonic wave with > 1 MHz frequency.[4] However, it is difficult to observe such a phenomenon with audible sound, having a lower frequency in the range of 20–20,000 Hz, whose wavelength is substantially longer than the molecular scale length. A few examples, including our studies, have been known for the audible sound-responsive nanomaterial that in the future may develop voice-controllable molecular machines and devices.[6–8] We have reported that supramolecular nanofibres, composed of porphyrin, anthracene, or azobenzene derivatives, hydrodynamically align in solutions by sensing fluid flows generated by audible sound vibrations, and output induced linear dichroism (LD).[6,7] When the supramolecular nanofibres are long enough to average local effects of the Brownian motions of the solvent molecules, they react to weak sheared flows generated by the sound vibration. To evolve such nanoarchitectures, in this study we designed a novel audible sound-responsive photochromic nanofibre capable of switching reversibly the wavelength of the sound-induced LD with UV and visible light. No example has been reported for such multi-stimuli responsive nanoarchitecture that brings about the dynamic alignment and colour change in response to the sound and light.

We have previously reported an azobenzene derivative, bearing *N*-phenyl amide groups with long alkyl chains, whose *trans–cis* photoisomerization reversibly changes its self-assembly in a solution, to give twisted supramolecular nanofibres and amorphous aggregates, respectively.[7] When the sample solution is exposed to audible sound, the former assembly shows an LD response caused by its hydrodynamic orientation, but the latter one, which can not orient in the fluid flows, is LD silent. UV and visible light, thus, reversibly turn its capability of acoustic alignment in a solution on and off through photoconversions between the fibrous and the amorphous nanostructures. We herein designed a diarylethene derivative **DEU** (Scheme 1), bearing diphenyl urea groups appending long alkyl chains, with an expectation that it could form a bifunctional supramolecular nanofibre capable of causing the acoustic alignment and photochromism without structural deformations (Fig. 1). The diarylethene, when adopting an anti–parallel conformation, is known to undergo open–closed ring photoisomerization that occurs even in its crystal form without disrupting its crystal structure.[9,10,11] Some supramolecular polymers composed of the diarylethene derivatives are actually known to show such photochromic behavior.[12]



Scheme 1 Photoisomerizations of **DEU** with UV and visible lights.

DEU was designed to form a supramolecular nanofibre through directional 1D assembly owing to the intermolecular hydrogen bonding of the urea groups and Van der Waals interactions of the long alkyl chains. It was synthesized through a coupling reaction of 1-iodophenyl-3,4,5-tris(dodecoxyl)phenylurea and 1,2-bis(5-iodo-2-methyl-3-thienyl)perfluorocyclopentene (see Supporting

Information).[12] ^{1}H NMR spectrum of **DEU**, taken in $CDCl_3$ at 20 °C, showed that the ratio of open and closed forms is 94 : 6, determined from the integral ratio of δ = 2.03 and 2.12 ppm, corresponding to the attached methyl group to a thiophene ring (Fig. S1a). When a sample solution with a concentration of 1.1 mM was exposed to 365 nm UV-light from a light source of 500 W xenon lamp for 2.5 h at 20 °C, **DEU$_{open}$** decreased with increasing **DEU$_{closed}$** to a changed ratio of 29 : 71 (Fig. S1b). The ratio of **DEU$_{closed}$** increased by decreasing the sample concentration. The absorption spectrum of **DEU** before and after photoirradiation provided the lowest energy absorption bands at λ_{max} = 312 and 602 nm, respectively, originating from the open and closed form, respectively (Fig. S2). **DEU$_{closed}$**, then, reversed to **DEU$_{open}$** almost quantitatively upon photoirradiation with 580 nm visible light.

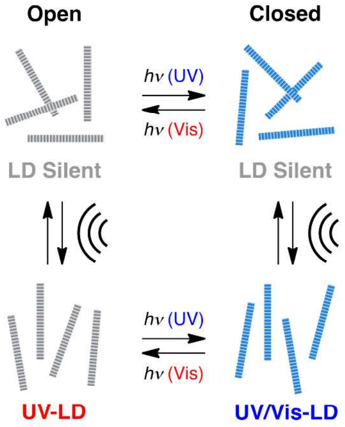


Fig. 1 Concept for sound-induced alignment and photochromism of the **DEU** supramolecular nanofibres.

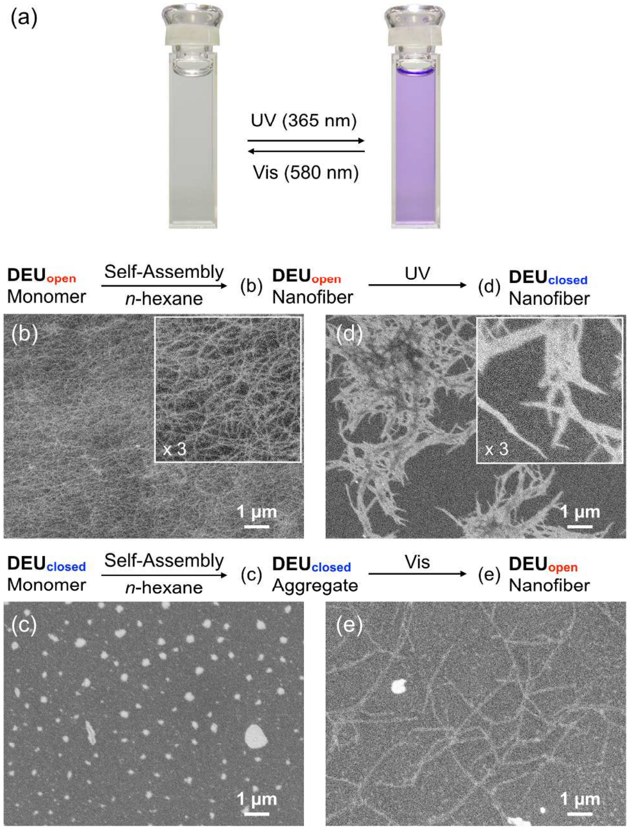


Fig. 2 (a) Photochromism of a *n*-hexane solution of the **DEU** supramolecular nanofibre upon photo-irradiations. (b) and (c) SEM images of air-dried samples prepared upon 130-fold dilution of $CHCl_3$ solutions of **DEU$_{open}$** and **DEU$_{closed}$**, respectively, with *n*-hexane to the concentration of 2.2 × 10^{-5} M. (d) and (e) SEM images of air-dried samples prepared upon photo-irradiation of their sample solutions with (c) 365 nm and (e) 580 nm light, respectively. The sample solutions were deposited on a specimen grid covered with a thin carbon support film.

Although a solid sample of **DEU$_{open}$** was hardly soluble in nonpolar solvents, it could be solubilized into *n*-hexane through a procedure upon 130-fold dilution of 1.7 × 10^{-3} M chloroform solution of **DEU$_{open}$** with *n*-hexane (Fig. 2a, left). Dynamic light scattering (DLS) measurement of the sample with the concentration of 2.2 × 10^{-5} M showed that **DEU$_{open}$** forms nanoscale aggregates having an average hydrodynamic radius of 5.8 × 10^3 nm with a size-distribution in the range of 2.5 × 10^3–4.3 × 10^4 nm (Fig. S3a). The SEM of the sample, prepared through a drop cast of the *n*-hexane solution of **DEU$_{open}$** onto a specimen grid covered with a thin carbon support film, revealed the presence of nanofibres with 40–80 nm diameters (Fig. 2b). When the sample was exposed to 365 nm UV light for 20 min, it brought about photochromism that changed the colour of the sample solution from colourless to purple. (Fig. 2a, right). Here, the ratio of open and closed forms could be estimated to be 7 : 93 by absorption spectroscopy (Fig. S4). SEM images of the resulting sample solution, showed the presence of the nanofibres, having larger needle-like structures (Fig. 2d). DLS measurement of the sample solution actually showed 1.6-fold enlargement of the average radius of the assemblies (Fig. S3b). The ring-closure reaction of the diarylethene unit may have caused the structural hardening of the polymer framework, which accelerated the bundling of the polymers. However, in sharp contrast, the sample solution prepared upon dilution of a $CHCl_3$ solution containing dominantly **DEU$_{closed}$** with *n*-hexane showed mainly nanoscale particles in SEM (Fig. 2c). DLS measurement actually showed that the sample included smaller aggregates, having an average radius of 200 nm with a size-distribution in the range of 160–250 nm (Fig. S5). The heterogeneous assemblies formed through mixing (*R*, *R*) and (*S*, *S*) enantiomers of **DEU$_{closed}$** may prevent the directional 1D assembly. The nanofibres, however, formed again upon exposing this sample solution to the 580 nm visible light that causes photoisomerization

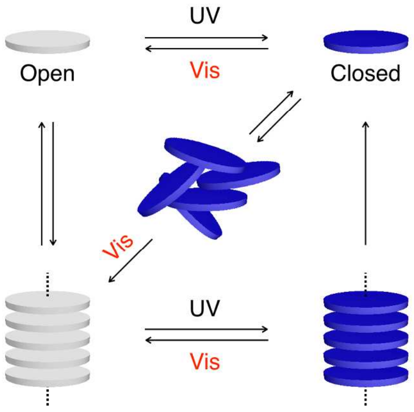


Fig. 3 Schematic illustration of the self-assembly and the photochromism of DEU.

to **DEU$_{open}$** (Fig. 2e). From these results, the photochromism and self-assembling behaviour of **DEU** can be schematically summarized in Fig. 3.

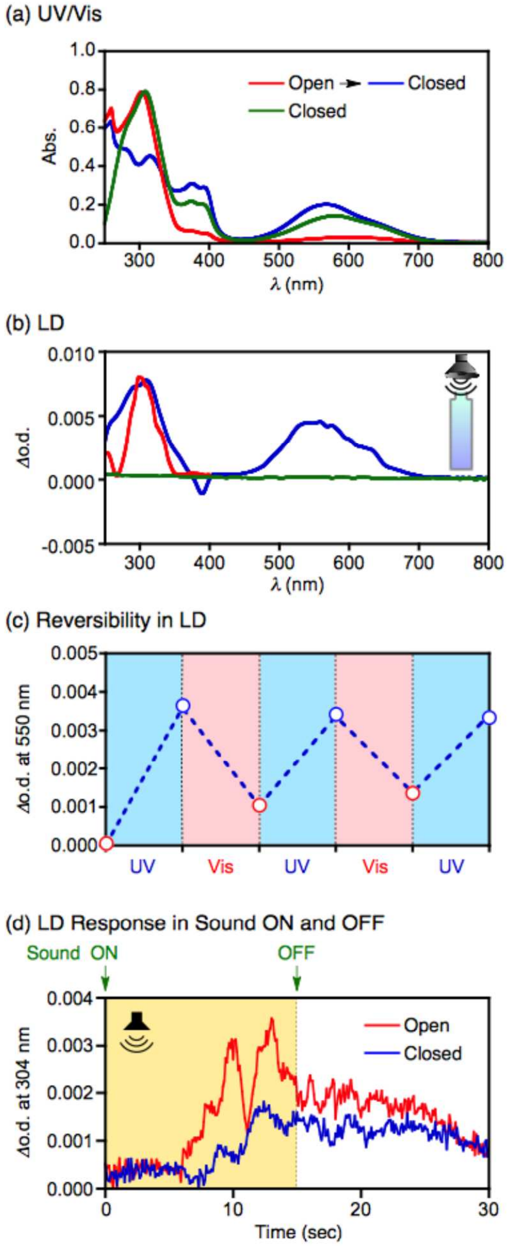


Fig. 4 (a) Absorption and (b) acoustic LD spectroscopies of the **DEU** supramolecular nanofibres before and after photo-irradiation with 365 nm and 580 nm light (red and blue curves, respectively), and the **DEU$_{closed}$** particle (green curve). (c) Reversible changes of the sound-induced LD monitored at 550 nm through sequential photo-irradiations with the UV and visible light for 20 min. (d) Time course profiles of changes in LD intensities of a solution of self-assembled **DEU** nanofibres before and after the photoisomerization upon exposure to 120 Hz sound wave for 15 sec. Solvent; *n*-hexane, [**DEU**] = 2.2×10^{-5} M, temperature; 20 °C, sound frequency and amplitude; 120 Hz and 13.5 Pa, respectively.

We herein noticed that the lowest energy absorption bands of the supramolecular nanofibres of **DEU$_{open}$** and **DEU$_{closed}$**, taken in *n*-hexane solution, are blue-shifted to λ_{max} = 304 and 567 nm, respectively (Fig. 4a, red and blue curves, respectively), in comparison with those of the non-assembled **DEU$_{open}$** and **DEU$_{closed}$** in $CHCl_3$, described above (Fig. S2). On the other hand, the **DEU$_{closed}$** particles showed a smaller shift in the corresponding absorption band with λ_{max} = 582 nm (Fig. 4a, green curve). Infinite dual hydrogen bonding networks of the urea groups of **DEU** in the assembly may allow a face-to-face arrangement of the diarylethene components, resulting in the blue-shift of the absorption band.[13] Judging from this result, and with the photochromic behaviour of the **DEU** nanofibre described above, **DEU$_{open}$** may form a *H*-aggregated supramolecular polymer with an anti–parallel conformation.

Supramolecular nanofibre, having a long thin linear structure, can dynamically align in solutions by sensing fluid flows generated by audible sound vibrations.[6,7] The mechanism of the alignment is such that the nanofibres react to velocity gradients in the media occurring in the crossing areas of the downward and upward flows, and by the laminar flows generated around the glass surfaces of the vessel due to the sound-induced fluid flows. The supramolecular nanofibre aligned in the solution shows LD response.[14,15] We conducted the LD spectral measurements for a *n*-hexane solution of the self-assembled **DEU** upon exposure to sinusoidal audible sound, which generates fluid flows including a primary oscillatory flow and a secondary steady flow in the solution.[16] The LD spectrometer in this study was equipped with a 12 × 12 × 44 mm^3 quartz optical cuvette, having a ϕ10 × 10 mm cylindrical neck (outer diameter), composed of 1 mm-thick quartz glass, which was filled with a solution of **DEU**. Although the *n*-hexane solution containing the self-assembled **DEU$_{open}$** at 20 °C showed no LD response without irradiation of the audible sound (Fig S6), the induced LD spectrum appeared in the UV region with λ_{max} = 304 nm upon exposure to 120 Hz sound with a sound pressure level of 13.5 Pa (Fig. 4b, red curve). Interestingly, when the **DEU$_{open}$** nanofibre was converted to the **DEU$_{closed}$** nanofibre upon irradiation with UV light, the sound-induced LD appeared in UV/visible region with λ_{max} = 304 and 582 nm (Fig. 4b, blue curve, and Fig S6). The sample solution reversibly switched the UV-LD and UV/Vis-LD upon irradiation of visible and UV light, respectively (Fig. 4c). The LD intensities were, however, gradually decreased probably due to photochemical breaking of the diarylethene component and/or deformations of the linear self-assembled structures. As expected, no LD response was observed with the sample containing the **DEU$_{closed}$** particles, since they had no capability to orient in the fluid flows (Fig. 4b, green curve). When monitoring the LD response of the sample solution containing **DEU$_{open}$** nanofibre at 304 nm, and turning the sound on and off, the nanofibres respond to the rise and fall of the fluid flows with an induction time of 9 sec (Fig. 4d, red curve). On the other hand, the sample, after photo-conversion to **DEU$_{closed}$** nanofibre, showed a relatively slower induction time of 12 sec (Fig. 4d, blue curve). With the higher concentration of **DEU** (3.3×10^{-5} M), which allows for the formation of larger assemblies, the induction time for the acoustic alignment of **DEU$_{open}$** nanofibre increased to 13 sec (Fig. S7). However, no notable ON–OFF response was observed for the sample after the conversion to **DEU$_{closed}$** nanofibre. The results are quite reasonable in that the observed acoustic alignment is the specific function of small nanofibres having a long thin linear structure. This gives it an advantage in sensing weak fluid flows that cause the hydrodynamically induced orientations.

In this study we have succeeded in synthesizing a bifunctional diarylethene supramolecular nanofibre capable of showing both photochromism and sound-induced alignment in a solution. The

DEU nanofibre in a solution shows induced LD when exposed to 120 Hz audible-sound, and reversibly switches to UV-LD and UV/Vis-LD upon photo-irradiation with visible and UV light, respectively. This is the multi-stimuli responsive intelligent nanoarchitecture that brings about the alignment and colour change in response to sound and light.

The present work was sponsored by Grants-in-Aid for Scientific Research (B) (No. 25286017) and Challenging Exploratory Research (No. 26620066) from the Ministry of Education, Science, Sports, and Culture, Japan.

Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

1 For reviews: (a) F. Ciardelli, G. Ruggeribc and A. Pucci, *Chem. Soc. Rev.*, 2013, **42**, 857; (b) L. D. Zarzar and J. Aizenberg, *Acc. Chem. Res.*, 2014, **47**, 530; (c) Z. Qi and C. A. Schalley, *Acc. Chem. Res.*, 2014, **47**, 2222; (d) H. K. Bisoyi and Q. Li, *Acc. Chem. Res.*, 2014, **47**, 3184; (e) M. Yan, S. K. P. Velu, M. Maréchal, G. Royal. J. Galvez and Pierre Terech, *Soft Matter.*, 2013, **9**, 4428.

2 H. Kawamura, *Kagaku*, (Iwanami Shoten, Publisher) 1938, **7**, 6–7 [in Japanese].

3 (a) R. Ozaki, T. Shinpo, M. Ozaki and H. Moritake, *Jpn. J. App. Phys.*, 2007, **46**, 489; (b) S. N. Cha, J. Seo, S. M. Kim, H. J. Kim, Y. J. Park, S. Kim and J. M. Kim. *Adv. Mater.*, 2010, **22**, 4726.

4 (a) K. Yasuda, T. Matsuoka, S. Koda and H. Nomura, *Jpn. J. Appl. Phys.*, 1994, **33**, 2901; (b) K. Yasuda, T. Matsuoka, S. Koda and H. Nomura, *J. Phys. Chem. B,* 1997, **101**, 1138; (c) H. Nomura, T. Matsuoka and S. Koda, *Pure. Appl. Chem.*, 2004, **76**, 97.

5 D. Huo and T. Kobayashi, *Chem. Lett.*, 2006, **35**, 776.

6 (a) A. Tsuda, Y. Nagamine, R. Watanabe, Y. Nagatani, N. Ishii and T. Aida, *Nat. Chem.*, 2010, **2**, 977; (b) R. Miura, Y. Ando, Y. Hotta, Y. Nagatani and A. Tsuda, *ChemPlusChem*, 2014, **79**, 516.

7 Y. Hotta, S. Suiko, J. Motoyanagi, H. Onishi, T. Ihozaki, R. Arakawa and A. Tsuda, *Chem. Commun.*, 2014, **50**, 5615.

8 S. Shoaee, J. Briscoe, J. R. Durrant and S. Dunn, *Adv. Mater.*, 2014, **26**, 263.

9 (a) M. Irie, *Chem. Rev.*, 2000, **100**, 1685; (b) S. Kobatake, K. Uchida, E. Tsuchida and M. Irie, *Chem. Commun.*, 2002, **38**, 2804.

10 (a) M. Irie, K. Uchida, T. Eriguchi and H. Tsuzuki, *Chem. Lett.*, 1995, **24**, 899; (b) S. Kobatake and M. Irie, *Bull. Chem. Soc. Jpn.*, 2004, **77**, 195.

11 (a) S. Pu, C. Zheng, Q. Sun, G. Liu and C. Fan, *Chem. Commun.*, 2013, **49**, 8036; (b) G. Liu, S. Pu and R. Wang, *Org. Lett.*, 2013, **15**, 980; (c) S. Pu, Z. Tong, G. Liu and R. Wang, *J. Mater. Chem. C*, 2013, **1**, 4726.

12 (a) M. Takeshita, M. Hayashi, S. Kadota, K. H. Mohammed and T. Yamato, *Chem. Commun.*, 2005, 761; (b) T. Hirose, M. Irie and K. Matsuda, *Chem. Asian J.*, 2009, **4**, 58; (c) S. Yagai, K. Ohta, M. Gushiken, K. Iwai, A. Asano, S. Seki, Y. Kikkawa, M. Morimoto, A. Kitamura and T. Karatsu, *Chem. Eur. J.*, 2012, **18**, 2244.

13 (a) F. Sun, F. Zhang, F. Zhao, X. Zhou and S. Pu, *Chem. Phys. Lett.*, 2003, **380**, 206; (b) S. Ghosh, X.-Q. Li, V. Stepanenko and F. Würther, *Chem. Eur. J.*, 2008, **14**, 11343; (c) L. Ma, Q. Wang, G. Lu, R. Chen and X. Sun, *Langmuir*, 2010, **26**, 6702.

14 (a) M. R. Hicks, J. Kowalski and A. Rodger, *Chem. Soc. Rev.*, 2010, **39**, 3380; (b) B. Nordén, A. Rodger and T. Dafforn, *Linear Dichroism and Circular Dichroism: A Textbook on Polarized-Light Spectroscopy,* 1st ed.; Royal Society of Chemistry: Cambridge, 2010.

15 (a) A. Tsuda, M. A. Alam, T. Harada, T. Yamaguchi, N. Ishii and T. Aida, *Angew. Chem. Int. Ed.*, 2007, **46**, 8198; (b) M. Wolffs, S. J. George, Z. Tomovic, S. C. J. Meskers, A. P. H. J. Schenning and E. W. Meijer, *Angew. Chem. Int. Ed.,* 2007, **46**, 8203; (c) Y. Ando, T. Sugihara, K. Kimura and A. Tsuda, *Chem. Commun.*, **2011**, *47*, 11748.

16 (a) J. Lighthill, *Journal of Sound and Vibration.,* 1978**, 61***,* 391; (b) A. Nowicki, T. Kowalewski, W. Secomski and J. Wójcik, *Eur. J. Ultrasound.*, 1998, **7***,* 73.