

Supporting Information for

Guest-responsive coherence time of radical qubits in a metal-organic framework

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Materials

All reagents were used as purchased unless otherwise noted. Naphthalene-2,3-diol, benzene-1,2-diamine, potassium dichromate, bromine, trifluoroacetic acid, and cesium carbonate were purchased from FUJIFILM Wako pure chemical. Acetic acid, hydrochloric acid, and potassium hydroxide were purchased from KISHIDA. 4-(methoxycarbonyl)phenylboronic acid and zirconium tetrachloride were purchased from TCI. PEPPSITM-IPr and 2,2,6,6-tetramethylpiperidine 1-oxyl free radical were purchased from Sigma Aldrich.

General characterizations

¹H-NMR spectra were measured on a Bruker AVANCE NEO 400 spectrometer using TMS as the internal standard. Elemental analysis was carried out by using a Yanaco CHN Corder MT-5 at the Elemental Analysis Center, Kyushu University. Powder X-ray diffraction (PXRD) patterns were measured on a Bruker D2 Phaser (Cu-K α , 30 kV 10 mA, 2 θ Range 2-50°, Step size 0.02°, scan speed 0.2 sec per step). Thermogravimetric analysis (TGA) curves were obtained on a Rigaku Thermo Plus EVO2 under N₂ (Range 25-500 °C, Heating rate 10 °C per min). N₂ adsorption isotherm measurements were carried out on a Bel BELSORP-max. Prior to gas adsorption experimentation, the sample was activated according to the typical procedure. The as-synthesized sample was solvent exchanged with chloroform (72 h) followed by thermal activation under vacuum at 120 °C for 10 hr. Mass spectrum was measured on Bruker Autoflex max MALDI-TOF MS mass spectrometer.

ESR spectroscopy

Steady state continuous wave electron spin resonance (CW-ESR) spectra were measured on a Bruker EMX 8/2.7 at X-band (~9.6 GHz) using a glass capillary (FPT-220, FUJISTON, diameter 2.2 mm, inner diameter 1.4 mm) placed into a 4 mm quartz ESR tubes.

Pulsed ESR measurements were performed on a Bruker E680 operated at X-band (~9.6 GHz) using a glass capillary (FPT-220, FUJISTON, diameter 2.2 mm, inner diameter 1.4 mm) placed into a 4 mm quartz ESR tubes. A Bruker standard dielectric resonator was used as a microwave resonator (ER4118X-MD5W) using TE011 mode. The microwave intensities were ~0.06 mW for time-resolved measurements unless otherwise noted. For pulsed ESR measurements, 1 kW amplified microwave irradiation was optimized to a fix $\pi/2$ pulse of 16 ns. Inversion recovery measurements were conducted using a three-pulse spin echo sequence. The first π pulse was irradiated, with an interval τ before the second $\pi/2$ pulse being varied. The third pulse irradiated after 0.2 μ s of interval, and then the echo signal followed after 0.2 μ s of interval was observed. T_1 was obtained by single exponential fitting of recovery curves. The echo decay measurements were conducted using a two-pulse spin echo sequence. The pulse interval τ between the first $\pi/2$ pulse and the second $\pi/2$ pulse was varied, and then the echo signal followed after 0.2 μ s of interval was observed. T_2 was obtained by single exponential fitting of decay curves. $\pi/2$ pulse and π pulse were fixed as 16 ns and 32 ns, respectively.

ESR sample preparation

MOF powder was activated by solvent exchange with chloroform followed by thermal activation at 120 °C under vacuum. The following guest molecules were introduced into activated DAT-MOF-4 as vapor: hexane, benzene, toluene, toluene-*d*₈, H₂O, and D₂O. The resulting powder samples were packed into a glass capillary (FPT-220, FUJISTON, diameter 2.0 mm, inner diameter 1.4 mm), degassed to remove oxygen at 77 K, and flame-sealed.

Synthesis of DATDBA

DATDBA was synthesized according to the reported procedure.¹

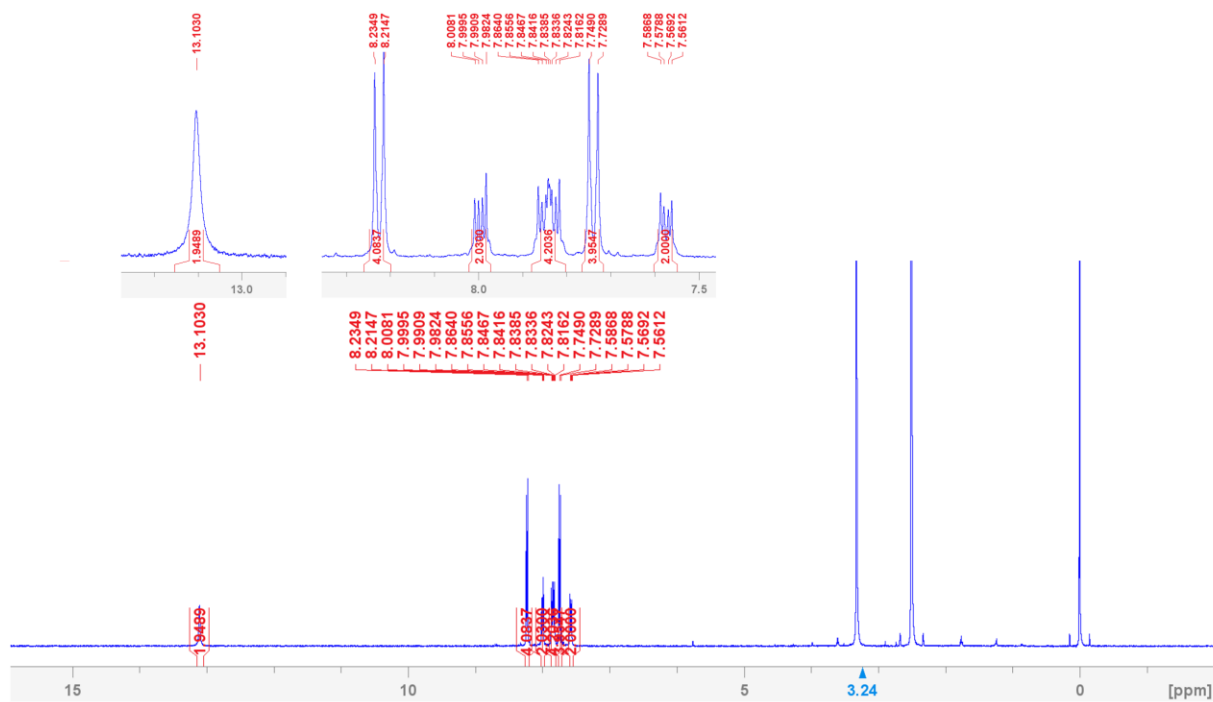


Fig. S1 ¹H-NMR spectrum of DATDBA in DMSO-*d*₆.

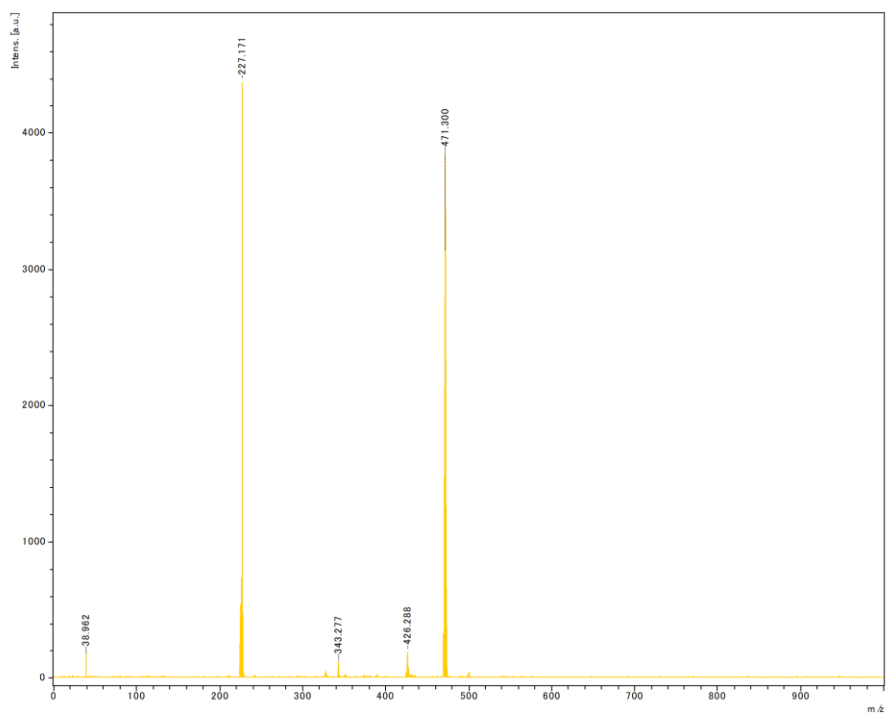


Fig. S2 MALDI-TOF-MS spectrum of DATDBA.

Synthesis of DAT-MOF-4

In a 13.5-mL screw-capped glass vial, ZrCl_4 (11.65 mg, 0.05 mmol) and trifluoroacetic acid (68 μL , 0.9 mmol) were dissolved in 5 mL of DMF, then DATDBA (23.52 mg, 0.05 mmol) was added followed by sonication and heating at 120 °C for 72 h in the oven. After cooling to room temperature, red powder-like crystals of DAT-MOF-4 were obtained. The obtained MOF powder was vacuum filtered, washed with 10 mL fresh DMF and vacuum dried at 50 °C for 1 h to obtain the as-synthesized DAT-MOF-4.

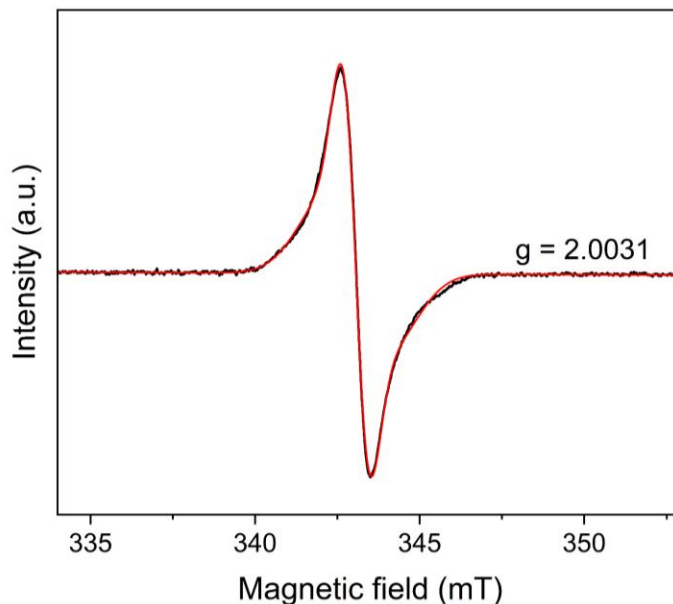


Fig. S3 Experimental CW-ESR spectrum of activated DAT-MOF-4 (black line) and simulated spectrum with two components (red line). CW-ESR simulations showed there were two components, which might reflect inhomogeneity of the paramagnetic sites. T_1 curves were also fitted with two components (Fig. S7b), which might correspond to the two components observed in the CW-ESR spectra. On the other hand, T_2 curves could be simulated with a single component (Fig. 4), probably because the second component could not be detected due to too short T_2 . Fitting of the spectra were performed with EasySpin (6.0.0-dev.53)². Simulation parameters; $g=2.003$ (fit), 7.66×10^{-6} (error), $lw=0.851$ (fit), 0.0036 (error), weight=1.0 (fixed) for the first component, $g=2.003$ (fit), 2.52×10^{-5} (error), $lw=2.088$ (fit), 0.0108 (error), weight=2.68 (fit), 0.0387 (error) for the second component.

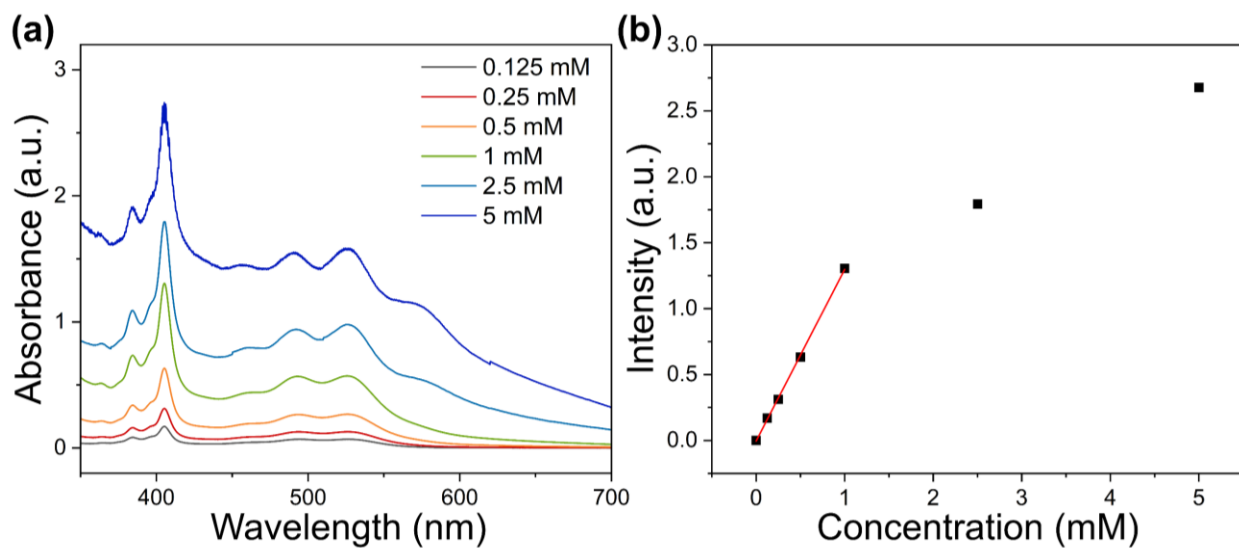


Fig. S4 (a) Concentration-dependent absorption spectra of DATDBA in THF at room temperature. (b) Beer-Lambert plot of DATDBA in THF at 405.4 nm. The fitted linear line (red) indicates DATDBA is molecularly dispersed in THF up to 1 mM at room temperature.

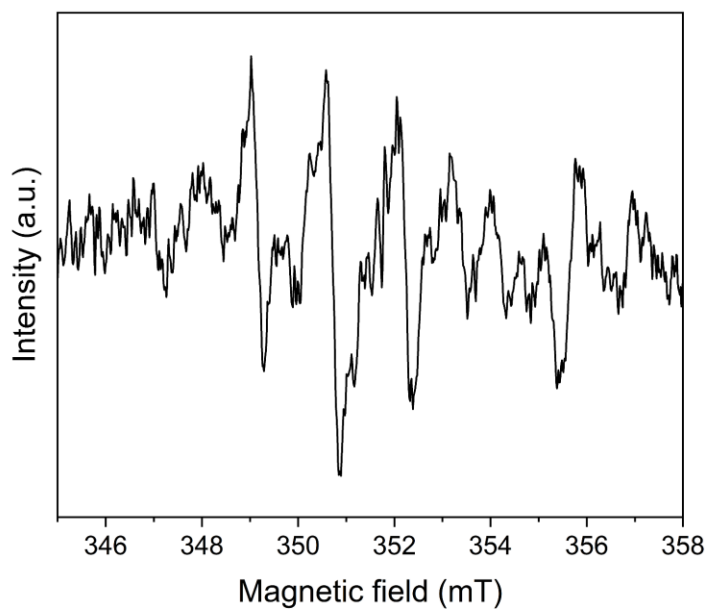


Fig. S5 CW-ESR spectrum of 1 mM DATDBA in THF. The microwave frequency was 9.8455 GHz.

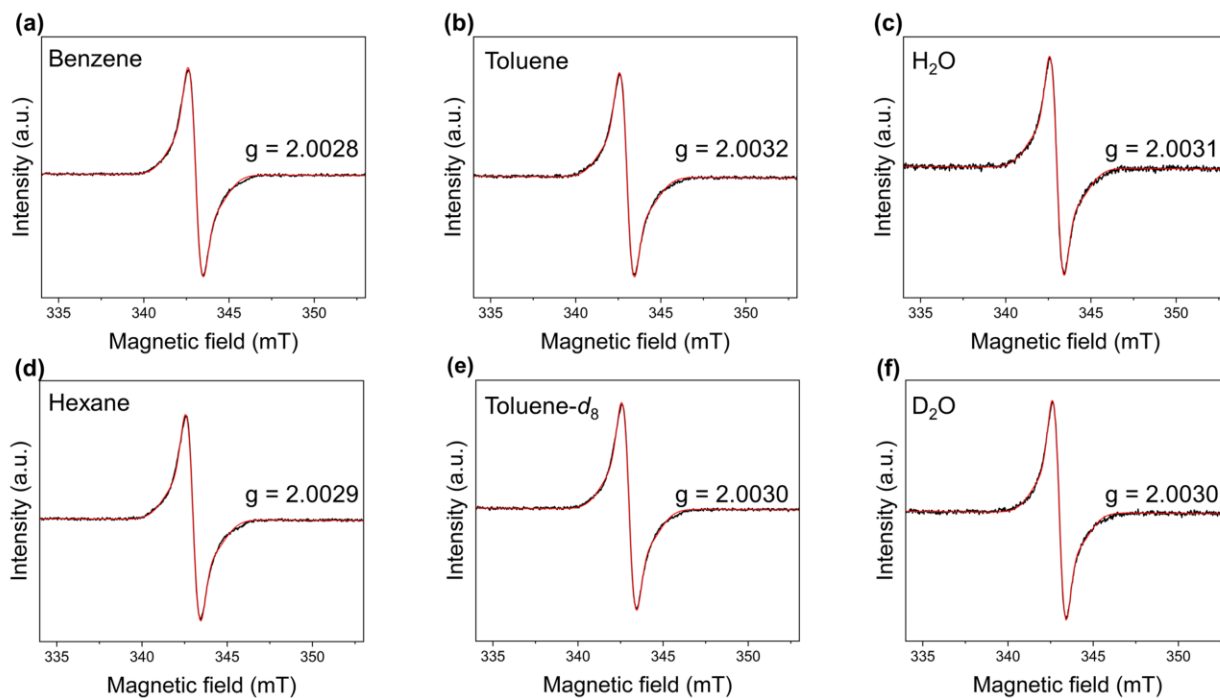


Fig. S6 Experimental CW-ESR spectra (black line) and simulated spectra (red line) of radicals in DAT-MOF-4 containing (a) benzene, (b) toluene, (c) H₂O, (d) hexane, (e) toluene-*d*₈, and (f) D₂O. The microwave frequency of each measurement was (a) 9.6168 GHz, (b) 9.6159 GHz, (c) 9.6160 GHz, (d) 9.6158 GHz, (e) 9.6157 GHz, and (f) 9.6162 GHz, respectively. All simulated spectra were fitted with two components as well as activated DAT-MOF-4.

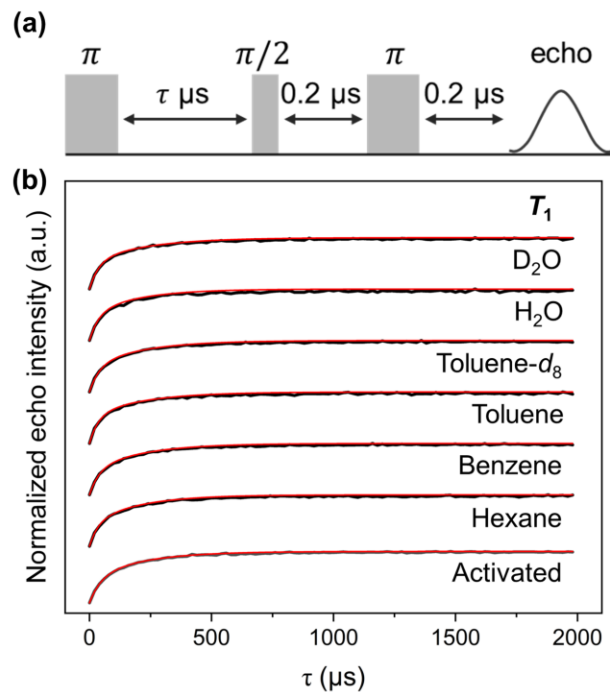


Fig. S7 (a) Sequence of inversion recovery of pulsed ESR for T_1 measurements. (b) Recovery of the echo intensity for activated DAT-MOF-4 and DAT-MOF-4 containing hexane, benzene, toluene, toluene- d_8 , H_2O , and D_2O . Double-exponential fitting curves and resulting T_1 values are also shown as red lines.

Table. S1 Double exponential fitting curves parameters of recovery of the echo intensity.

	$-A_1 \exp(-t/T_{1short}) - A_2 \exp(-t/T_{1long})$			
	A_1	T_{1short} (μs)	A_2	T_{1long} (μs)
Activated	0.457 ± 0.0257	45.8 ± 3.25	0.523 ± 0.0259	210.3 ± 7.88
Hexane	0.419 ± 0.0249	33.2 ± 3.03	0.552 ± 0.0240	195.5 ± 7.43
Benzene	0.452 ± 0.0238	38.0 ± 2.97	0.518 ± 0.0232	211.9 ± 8.16
Toluene	0.502 ± 0.0284	35.0 ± 3.16	0.460 ± 0.0271	217.0 ± 11.69
Toluene- d_8	0.474 ± 0.0247	39.4 ± 2.99	0.490 ± 0.0242	214.4 ± 8.97
H_2O	0.483 ± 0.0386	36.3 ± 4.17	0.474 ± 0.0380	195.0 ± 12.94
D_2O	0.513 ± 0.0231	37.3 ± 2.71	0.457 ± 0.0219	233.8 ± 10.49

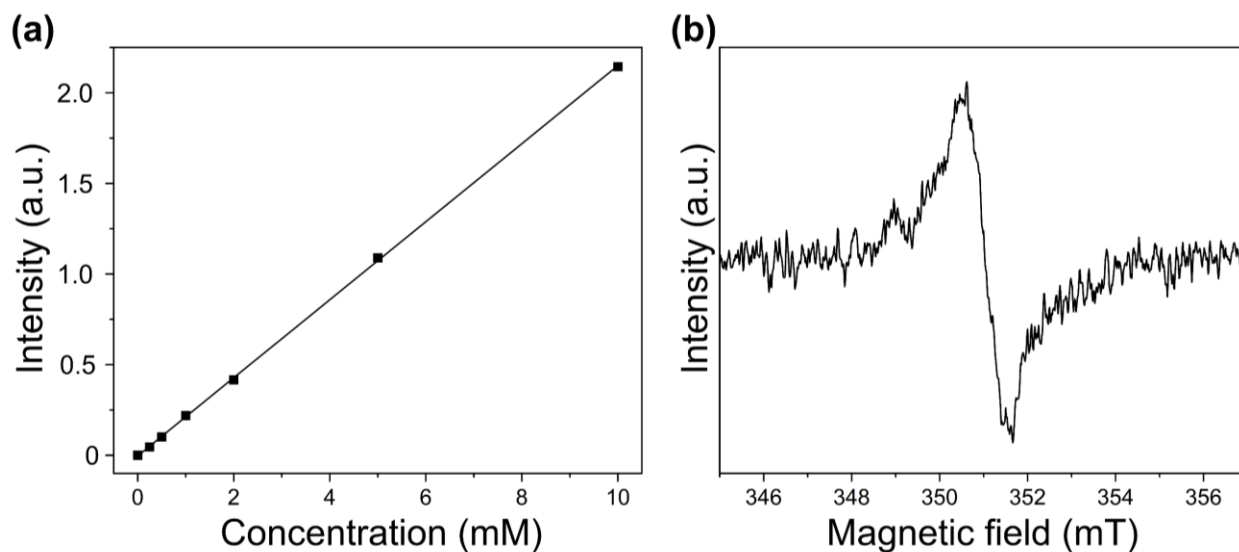


Fig. S8 (a) Calibration curve of TEMPO in toluene (0.25, 0.5, 1, 2, 5, 10 mM). (b) CW-ESR spectrum of 1.2 mg of DAT-MOF-4 in 10 μ L of toluene. The radical concentration in the MOF is estimated to be 0.059 mM from the calibration curve of the TEMPO solution. This means that 0.03 mol% of the DAT ligand in MOF is present as radicals, considering the formula weight of activated MOF (3490.18). This means that there is 1 radical per 139 unit cells, and since the unit cell length is 3.26 nm, the average distance between radicals is estimated to be about 17 nm.

References

1. H. Kouno, K. Orihashi, K. Nishimura, Y. Kawashima, K. Tateishi, T. Uesaka, N. Kimizuka and N. Yanai, *Chem. Commun.*, 2020, **56**, 3717-3720.
2. S. Stoll and A. Schweiger, *J Magn Reson*, 2006, **178**, 42-55.