

Magnetic field-sensitive radical pair dynamics in polymethylene ether-bridged donor-acceptor systems

Supporting Information

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Additional experimental details:

9,10-Dimethylantracene (DMAnt, Aldrich, 99%) was used as received, 9-methylantracene (MAnt, Aldrich, 98%) was recrystallized from ethanol. *N,N*-dimethylaniline (DMA, Aldrich, 99.5%) was distilled under reduced pressure and subsequently handled under an argon atmosphere. Butyronitrile (BN, Fluka, purum, 99%), propyl acetate (PA, Aldrich, 99.5%), propionitrile (EtCN, Aldrich, 99.5%) and acetonitrile (AN, Aldrich, 99.8%) were purified by distillation. 1,6-dibromohexane (1,6-DBH, Aldrich, 99%), 1,8-dibromooctane (1,8-DBO, Aldrich, 96%), 1,10-DBD: 1,10-dibromodecane (1,10-DBD, Aldrich, 98%), 1,16-HDDO: 1,16-hexadecanediol (1,16-HDDO, Aldrich, 97%), 2-[(4-dimethylamino)phenyl]ethanol (DMAPE, Aldrich, 99%) were used as received.

Extracted exciplex spectra:

The vibronic transitions with Gaussian band shape of the exciplex were extracted by employing a model as described in refs. [1] and [2]. Figure S1 gives the emission spectra of the exciplexes of MAnt-*n*-O-2-DMA ($n = 8, 10, 16$) in butyronitrile (BN, $\epsilon_s = 24.7$).

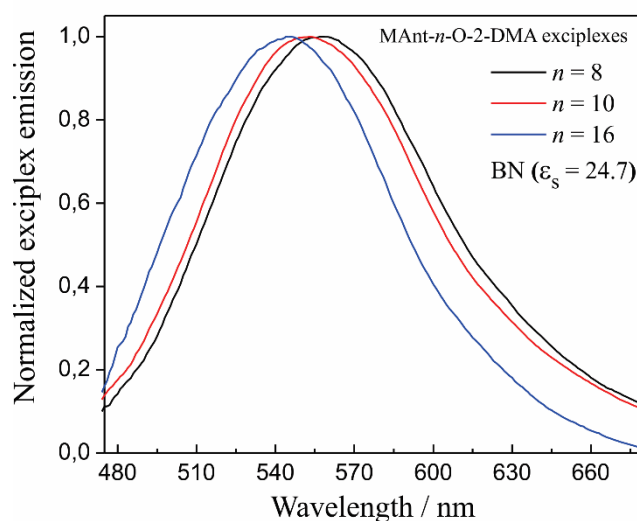


Figure S1: Extracted emission spectra of the exciplexes of MAnt-*n*-O-2-DMA in butyronitrile. The emission maximum is shifted hypsochromically as *n* increases.

Exciplex emission maxima:

A plot of the position of the exciplex emission maximum (in eV) as a function of the solvent polarity parameter Δf , defined in terms of the solvent dielectric constant (ϵ_s) and the refractive index (*n*) by $\Delta f = (\epsilon_s - 1)/(2\epsilon_s + 1) - (n - 1)/(4n^2 + 2)$, is given in Figure S2. Here, $n = 1.383$ is refractive index of PA/BN mixtures with ϵ_s within a range from 6 to 24.7. For $n = 8, 10$ and 16, the degree of charge transfer increases with decreasing length of the linker.

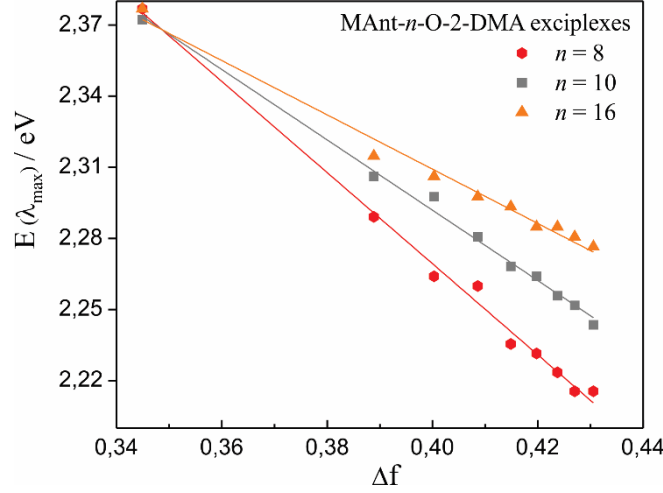


Figure S2: The position of the exciplex emission maximum (in eV) as a function of the solvent polarity parameter Δf for MAnt- n -O-2-DMA exciplexes in PA/BN mixtures of various dielectric constant ϵ_s in the range from 6 to 24.7.

Solution of eq. (2) in the semiclassical limit:

According to the semiclassical approximation, the hyperfine coupled nuclei are accounted for in terms of constant local magnetic fields $\hbar / (g_i \mu_B) \mathbf{N}_i$. In this approximation, the spin Hamiltonian is reduced to eq. (S1) with

$$\hat{H}_i = \left(\frac{g_i \mu_B B_0}{\hbar} \hat{e}_z + \mathbf{N}_i \right) \hat{\mathbf{S}}_i, \quad (\text{S1})$$

which is defined in the four-dimensional Hilbert space comprising the two electron spins only. \hat{e}_z is the unit vector in the z -direction. The effective hyperfine precession terms \mathbf{N}_i are assumed to be randomly oriented with norms, $N_i = \|\mathbf{N}_i\|$, sampled from the probability density function

$$p(N_i) = \left(\frac{\gamma_i^2}{4\pi} \right)^{3/2} \exp \left(-\frac{1}{4} \gamma_i^2 N_i^2 \right), \text{ where } \gamma_i^{-2} = \frac{1}{6} \sum_k \alpha_{i,k}^2 I_{i,k} (I_{i,k} + 1), \quad (\text{S2})$$

which is normalized with respect to integration over the entire \mathbf{N}_i -space, i.e. $4\pi \int_0^\infty p(N_i) N_i^2 dN_i = 1$. Here, $I_{i,k}$ denotes the nuclear spin quantum number of the k th nuclear spin in the i th radical. The time-averaged density operator is then given by

$$\hat{\rho} \approx \int \int \int \int \int \int dt d\theta_1 d\phi_1 dN_1 d\theta_2 d\phi_2 dN_2 \hat{\rho}(t, \mathbf{N}_1, \mathbf{N}_2) \sin(\theta_1) \sin(\theta_2) N_1^2 p(N_1) N_2^2 p(N_2), \quad (\text{S3})$$

where $\hat{\rho}(t, \mathbf{N}_1, \mathbf{N}_2)$ refers to the spin density operator obeying eq. (2) of the main document with \hat{H}_i given by eq. (S1) instead of eq. (4). The integrations over the orientations have been evaluated by Monte Carlo sampling and those over the norms using the Gauss-Hermite rule.

DFT-derived hyperfine coupling constants:

Tables S1 and S2 list the hyperfine coupling constants that have been used to calculate the MARY curves of MAnt-*n*-O-2-DMA.

Table S1. Used hyperfine coupling (hfc) constants for anthracene moiety. Hfcs have been calculated for 9-ethyl-10-methyl anthracene on the B3LYP/Def2-TZVPP/EPR-III level in Gaussian 16.³ The asymmetry of the substitution pattern has a negligible effect on the distribution of the spin density over the aromatic core. Closely agreeing hfc's have been collected in common groups of equivalent nuclei for convenience. The nuclear spin quantum number is denoted by *I*.

Type	<i>I</i>	hfc constant (mT)
4 × H (H1, H4, H5, H8)	1/2	-0.3184
4 × H (H2, H3, H6, H7)	1/2	-0.1376
5 × H (CH ₂ , CH ₃)	1/2	0.3908

Table S2. Used hyperfine coupling (hfc) constants for *N,N*-dimethylaniline moiety (DMA). Hfcs have been calculated for 2-[4-(dimethylamino)phenyl]ethanol. See Table S1 for details.

Type	<i>I</i>	hfc constant (mT)
6 × H (N(CH ₃) ₂)	1/2	1.1942
1 × N	1	0.8137
2 × H (-CH ₂ -)	1/2	0.5993
2 × H (-O-CH ₂ -)	1/2	-0.0617
2 × H (ortho)	1/2	-0.4601
2 × H (meta)	1/2	0.1197

Tentative simulations of the MARY curve of MAnt-6-O-2-DMA:

Figure S3 depicts the tentative simulations of the MARY curve of MAnt-6-O-2-DMA.

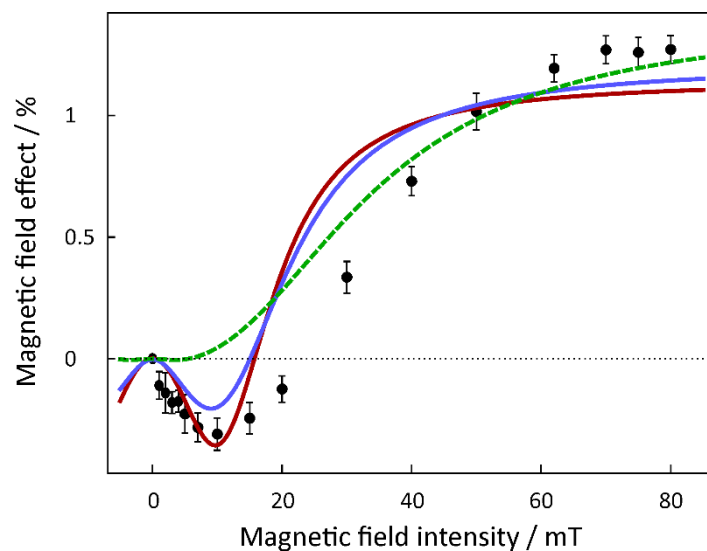


Figure S3: For MAnt-6-O-2-DMA, the one-sited model can only provide a tentative explanation of the experimental data. The figure shows simulations employing the following parameters: $J = -5$ mT and $k_S = 0.1$ ns⁻¹, $k_{ST} = 0.85$ ns⁻¹, $c \sim 12$ (red) or $k_S = 0.05$ ns⁻¹, $k_{ST} = 1.4$ ns⁻¹, $c \sim 15$ (blue). For larger k_{ST} , the agreement deteriorate: green: k_S same as for red but $k_{ST} = 3.7$ ns⁻¹ and $c \sim 7$.

Synthesis of polymethylene ether-linked acceptor / donor compounds:

The general procedure of the synthesis of polymethylene ether-linked donor /acceptor compounds containing the anthracene and *N,N*-dimethylaniline moieties MAnt-(CH₂)_n-O-(CH₂)₂-DMA (MAnt-*n*-O-2-DMA, *n* = 6, 8, 10, 16) is summarized in Figure S4.

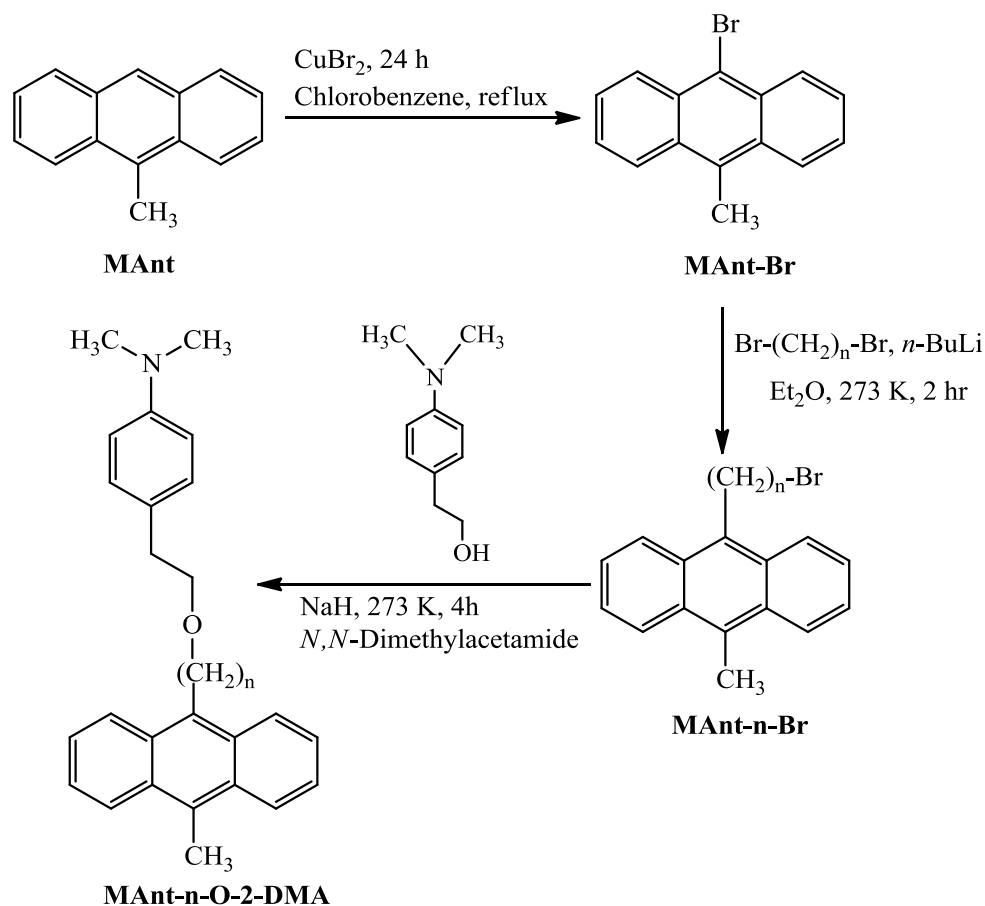


Figure S4: General procedure for the synthesis of the polymethylene ether-linked donor /acceptor compounds.

9-bromo-10-methylantracene (MAnt-Br): MAnt-Br was synthesized following the published procedure from ref. [4]: A stirred mixture of 9-methylantracene (960 mg, 5.0 mmole) and copper (II) bromide (2.24 g, 5.0 mmole) in chlorobenzene (200 ml) was heated under reflux for 24 h. The reaction mixture was filtered and concentrated *in vacuo*. The residue was then purified by chromatography on alumina eluting with *n*-hexane to obtain 9-bromo-10-methylantracene (0.83 g, 60 % yield). Formula: $\text{C}_{15}\text{H}_{11}\text{Br}$, Mp: 442-444 K. $^1\text{H-NMR}$ (CDCl_3 , 500 MHz) δ = 3.12 ppm (s, 3H, CH_3 -anthracene), 8.62-7.53 (8H, protons of anthracene ring). See $^1\text{H-NMR}$ spectrum Figure S5a.

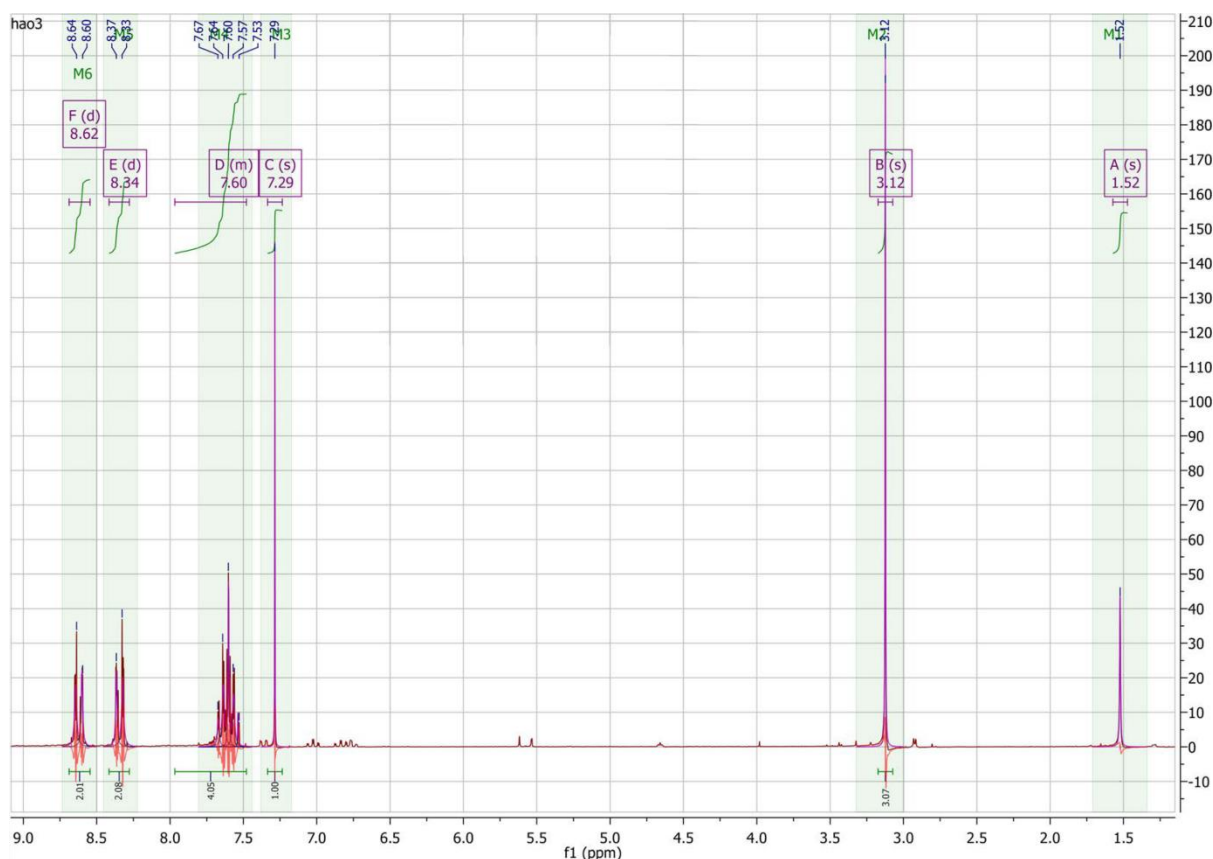


Figure S5a: ^1H -NMR spectrum of 9-Bromo-10-methylantracene (MAnt-Br).

1-bromo-10-[9-(10-methyl)anthryl]decane (MAnt-10-Br):⁵ A 2.5 M solution (2.8 ml) of *n*-butyllithium in hexane was added dropwise to a solution of 9-bromo-10-methylantracene (1 g, 3.68 mmole) in dried diethyl ether (20 ml) under argon atmosphere in an ice bath to maintain a temperature of 273 K. The mixture was stirred at 273 K for 4h. After adding 3.4 g (11.33 mmole) of 1,10-dibromodecane at once, the mixture was stirred for another 30 minutes. Eventually, the reaction mixture was refluxed for 2 h in an oil bath. The resulting mixture was extracted by benzene (3 x 25 ml). The benzene phases were combined and washed with water (2 x 50 ml). The combined organic phases were dried over MgSO_4 overnight. The solution was concentrated *in vacuo*. The residue was absorbed on silica gel and purified by column chromatography eluting with *n*-hexane to give MAnt-10-Br (0.78 g, 52% yield). Formula: $\text{C}_{25}\text{H}_{31}\text{Br}$, Mp: 350-351 K. ^1H -NMR (CDCl_3 , 500 MHz) δ = 3.12 ppm (s, 3H, CH_3 -anthracene), 8.37-7.51 (8H, protons of anthracene ring, 3.43 (t, 2H, $-\text{CH}_2\text{-Br}$), 3.62 (m, 2H, $-\text{CH}_2\text{-anthracene}$), 1.96-1.36 (m, 16H, protons of chain). The ^1H -NMR spectrum is shown in Figure S5b.

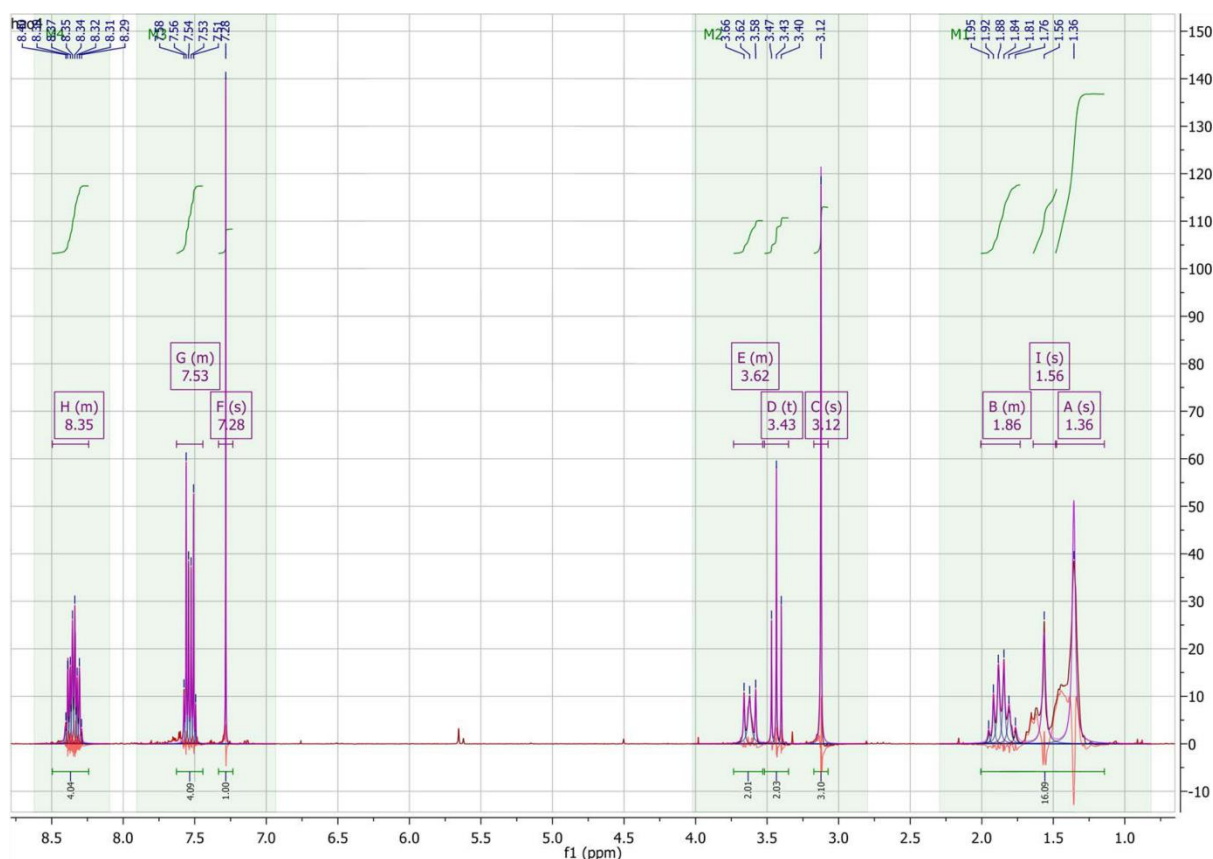


Figure S5b: ^1H -NMR spectrum of 1-bromo-10-[9-(10-methyl)anthryl]decane (MAnt-10-Br).

2-[4-(dimethylamino)phenyl]ethyl 10-[9-(10-methyl)anthryl]decyl ether (MAnt-10-O-2-DMA):⁶ 9-Bromo-10-methylantracene (MAnt-10-Br) (0.65 g, 1.58 mmole) and 2-[(4-dimethylamino)phenyl]ethanol (0.56 g, 3.39 mmole) were added to solution of 0.57 g NaH (60% oil suspension) in *N,N*-dimethylacetamide (15 mL). The mixture was stirred for 4h in an ice bath at 237 K, before extracting it with benzene (3×15 mL). The combined benzene phases were washed with cold water (3×20 mL) and dried over MgSO_4 overnight. The solvent was removed *in vacuo*. The product was isolated by column chromatography on silica gel with *n*-hexane and a *n*-hexane/ethyl acetate mixture (95:5) as eluting solvents to obtain MAnt-10-O-2-DMA (0.25 g, 38% yield). Formula: $\text{C}_{35}\text{H}_{45}\text{ON}$, MS (EI) m/z 495.35 (M^+ , 100), Mp: 328-329 K. ^1H -NMR (CDCl_3 , 500 MHz) δ = 8.50-7.50 ppm (8H, protons of anthracene ring), 7.50-7.10 (4H, protons of benzene ring), 3.61 (4H, $-\text{CH}_2-\text{O}-\text{CH}_2-$), 3.45 (2H, $-\text{CH}_2-\text{DMA}$), 3.12 (3H, CH_3 -anthracene), 2.95 (6H, $(\text{CH}_3)_2\text{N}-$), 2.8 (2H, $-\text{CH}_2$ -anthracene), 2.0-1.2 (16H, protons of chain). Proton-decoupled ^{13}C -NMR (CDCl_3 , 125 MHz) δ = 134-122 ppm (20C, aromatic carbons), 70-74 (4C, $-\text{CH}_2-\text{O}-\text{CH}_2-$ and $-\text{N}(\text{CH}_3)_2$), 35-36 (3C, CH_3 -anthracene, $-\text{CH}_2$ -anthracene and $-\text{CH}_2$ -benzene), 14-32 (8C, methylene carbons). The ^1H , ^{13}C -NMR and MS spectra are given in Figure S5c-e.

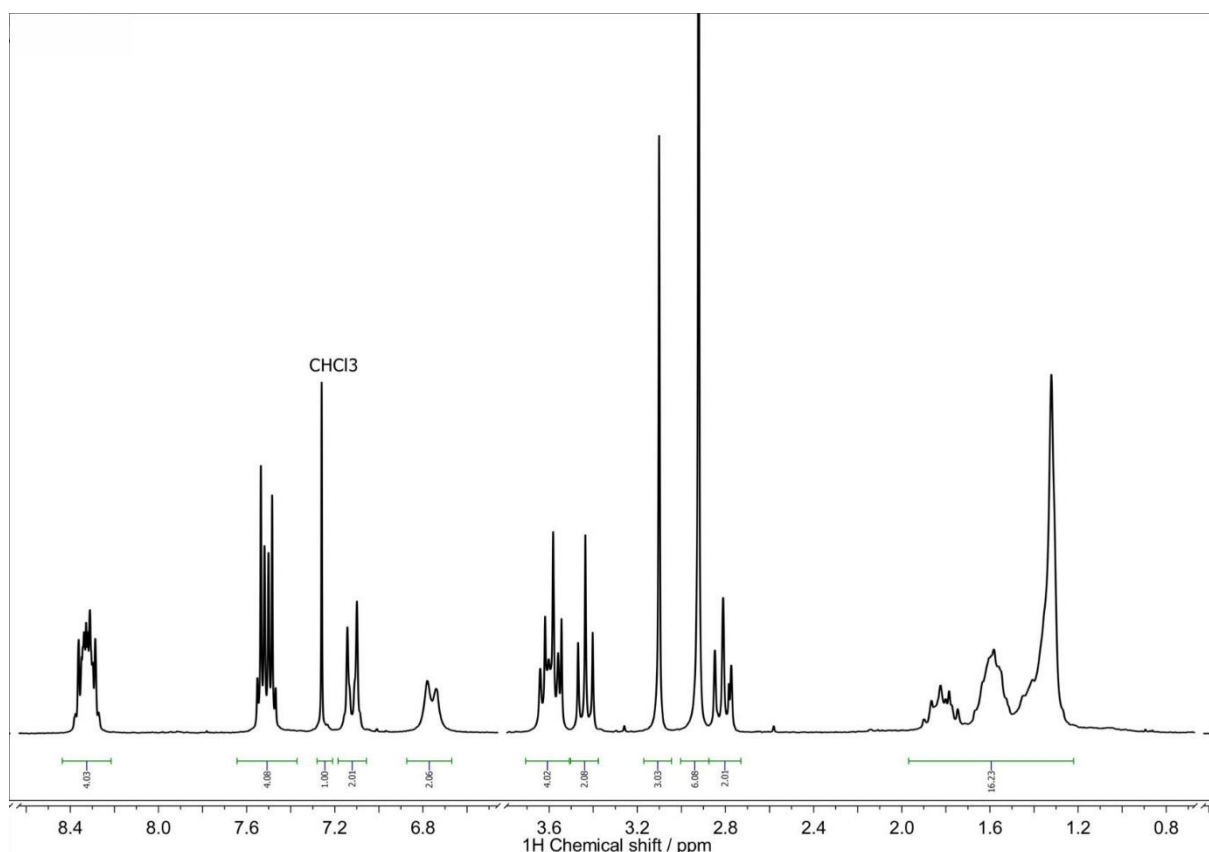


Figure S5c: ^1H -NMR spectrum of 2-[4-(dimethylamino)phenyl]ethyl 10-[9-(10-methyl)anthryl]decyl ether (MAnt-10-O-2-DMA).

1,16-dibromohexadecane (1,16-DBHD): the starting material 1,16-DBHD is not commercially available. 1,16-DBHD was synthesized by the following procedure:⁷ To a stirred solution of *N*-bromosuccinimide (2.75 g, 15.45 mmole) in 50 ml of tetrahydrofuran (THF) at 273 K, a solution of triphenylphosphine (4.06 g, 14.59 mmole) in 50 ml of THF was added dropwise. After reaching room temperature a solution of hexadecane-1,16-diol (1.0 g, 3.87 mmole) in 10 ml of THF was also added dropwise. The mixture was heated to 328 K for 2.5 h. The solvent was evaporated under vacuum. Water was added to the residue and the solution was extracted with diethyl ether. The organic phase was washed with water, dried with MgSO_4 , filtrated and then concentrated *in vacuo*. Flash chromatography of the resulting solid with *n*-heptane as eluent gave 1,16-dibromohexadecane (0.82 g, 55% yield) as a white solid. Mp: 329-330 K. 1,16-DBHD was used to synthesize MAnt-16-O-2-DMA.

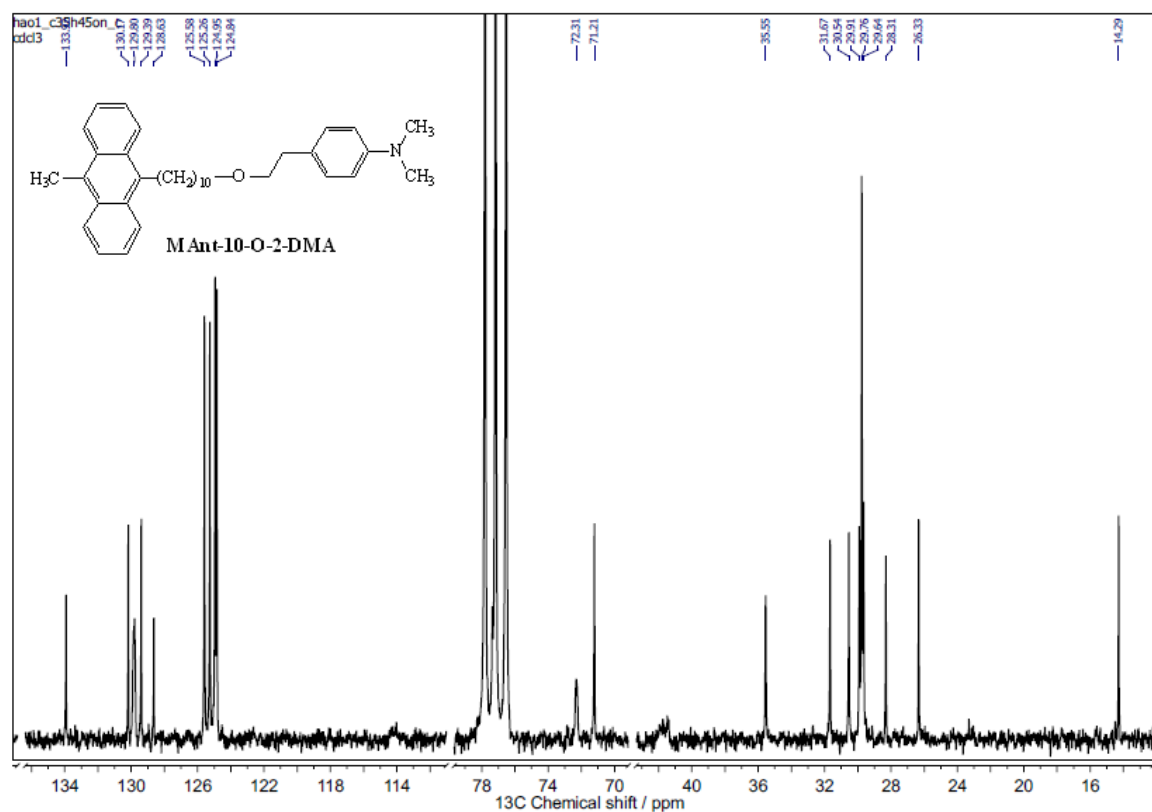


Figure S5d: Proton-decoupled ¹³C-NMR spectrum of 2-[4-(dimethylamino)phenyl]ethyl 10-[9-(10-methyl)anthryl]decyl ether (MAnt-10-O-2-DMA).

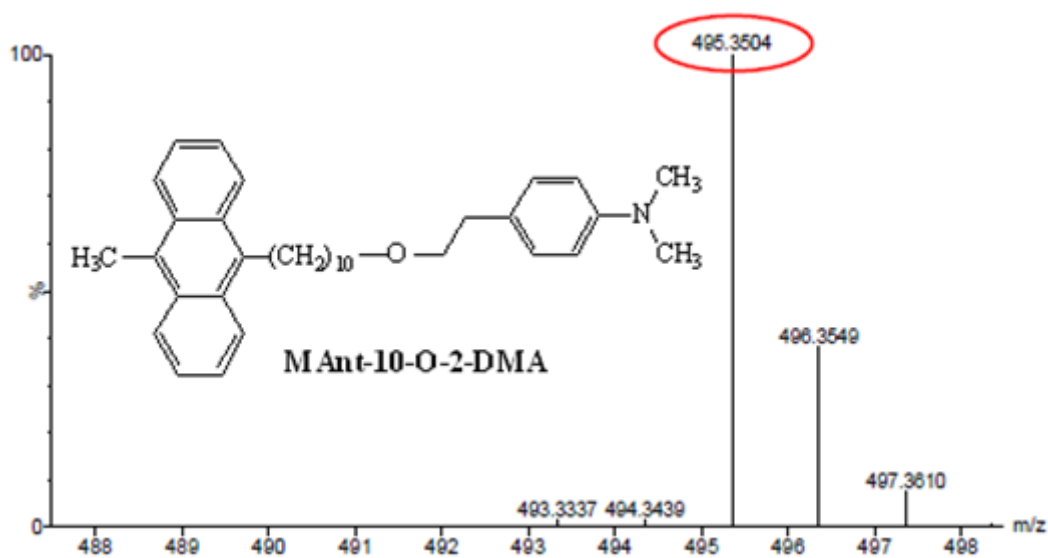


Figure S5e: Mass spectroscopy spectrum of 2-[4-(dimethylamino)phenyl]ethyl 10-[9-(10-methyl)anthryl]decyl ether (MAnt-10-O-2-DMA).

Other compounds

The other chain-linked fluorophore/quencher pairs with different chain lengths (MAnt-*n*-O-2-DMA, *n* = 6, 8, 16) were prepared by the same synthetic procedure. The yields and melting points are summarized in Table S3. The ¹H, ¹³C-NMR and Mass spectra of the MAnt-*n*-O-2-DMA (*n* = 6, 8, 16) compounds are given in Figure S5f-j.

Table S3: Yields and melting points of MAnt-*n*-O-2-DMA (*n* = 6, 8, 16) compounds.

Compound	Yield (%)	Melting point (K)
MAnt-6-O-2-DMA	57	322-323
MAnt-8-O-2-DMA	49	344-345
MAnt-16-O-2-DMA	42	326-327

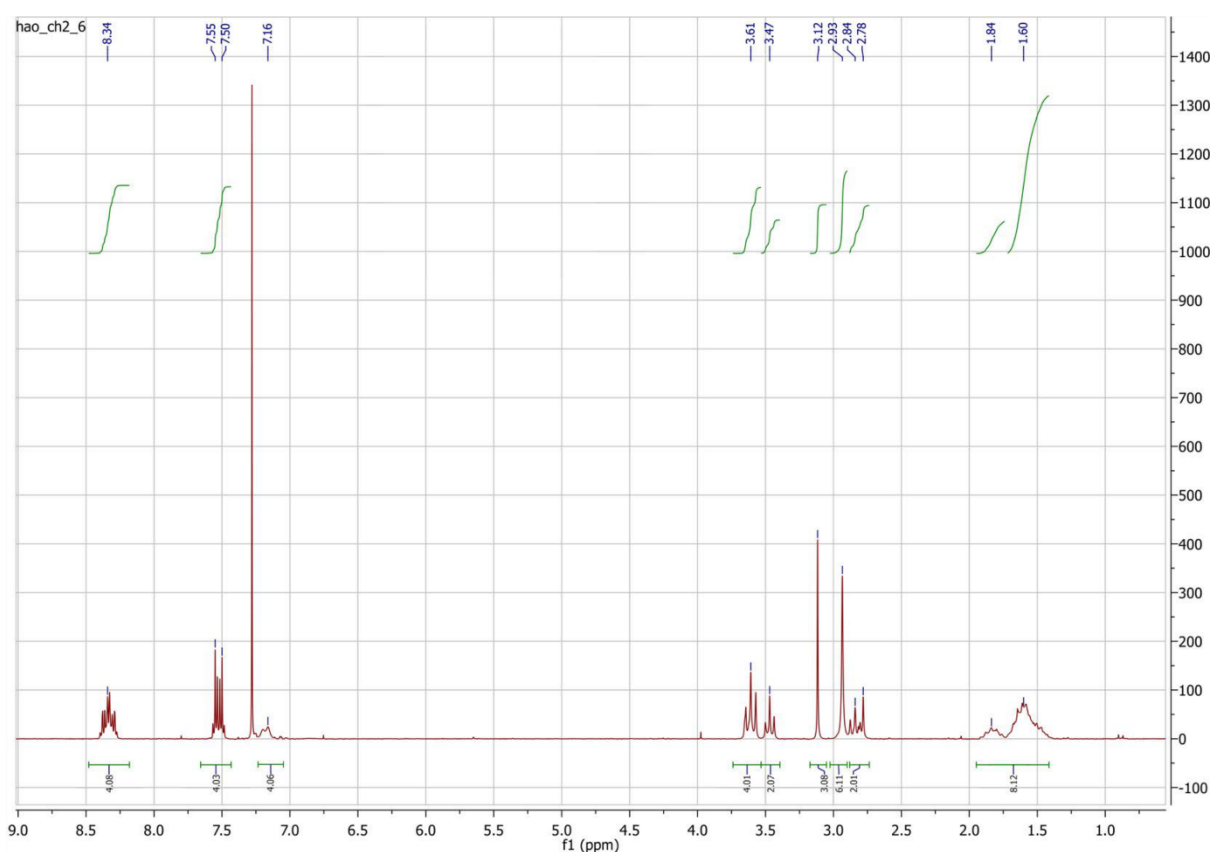


Figure S5f: ¹H-NMR spectrum of 2-[4-(dimethylamino)phenyl]ethyl 6-[9-(10-methyl)anthryl]hexyl ether (MAnt-6-O-2-DMA).

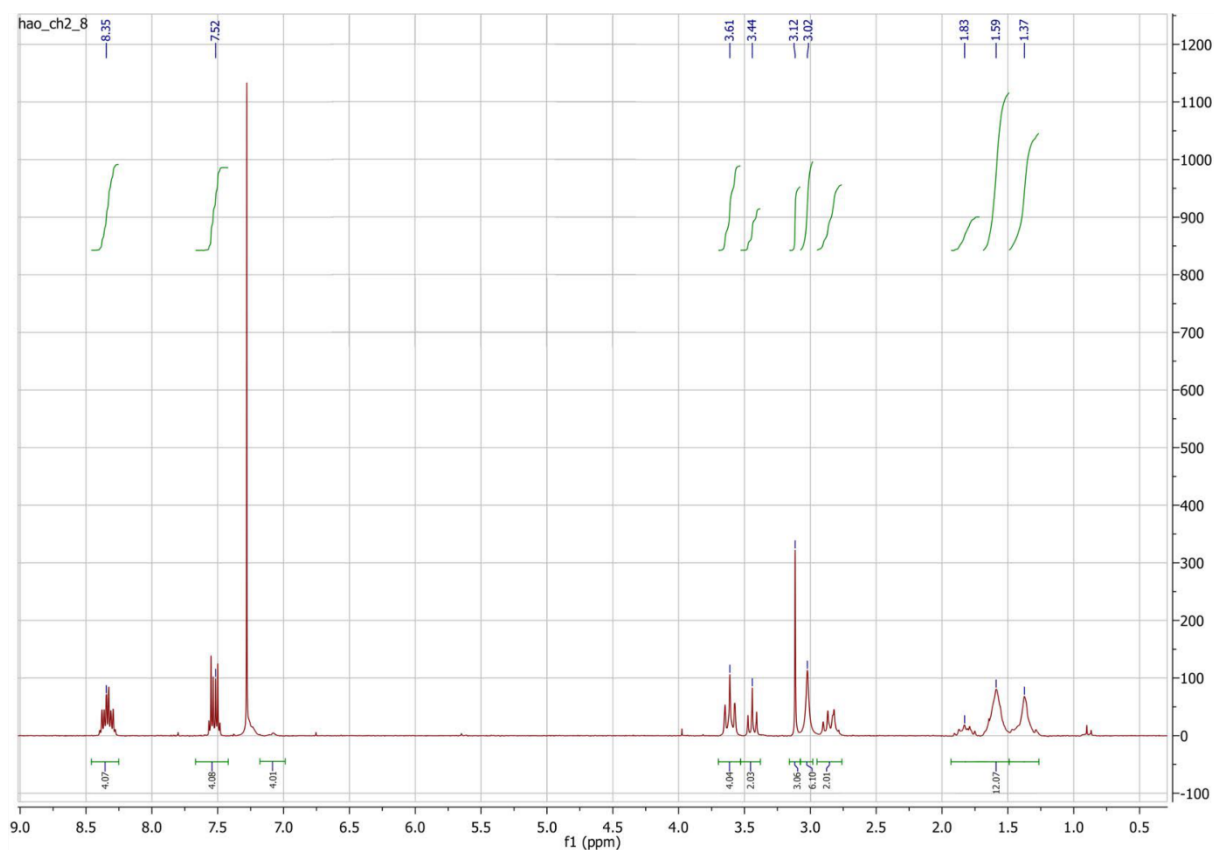


Figure S5g: ^1H -NMR spectrum of 2-[4-(dimethylamino)phenyl]ethyl 8-[9-(10-methyl)anthryl]octyl ether (Mant-8-O-2-DMA).

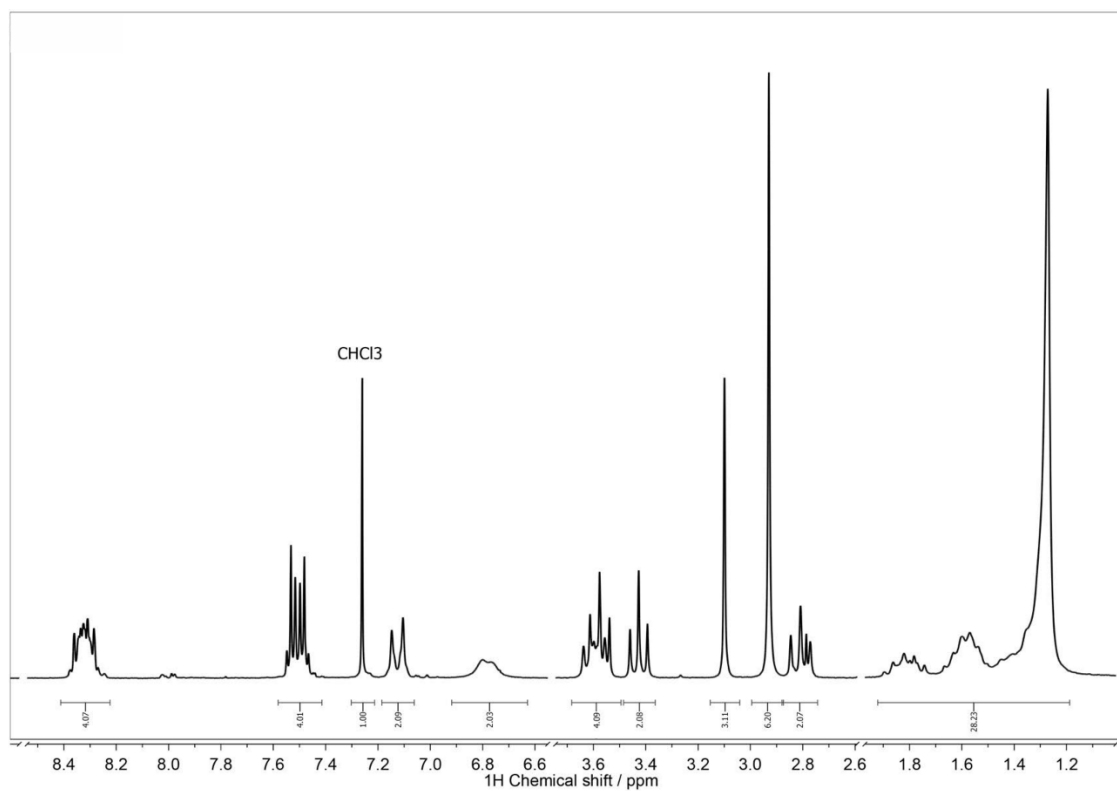


Figure S5h: ^1H -NMR spectrum of 2-[4-(dimethylamino)phenyl]ethyl 16-[9-(10-methyl)anthryl]hexadecyl ether (Mant-16-O-2-DMA).

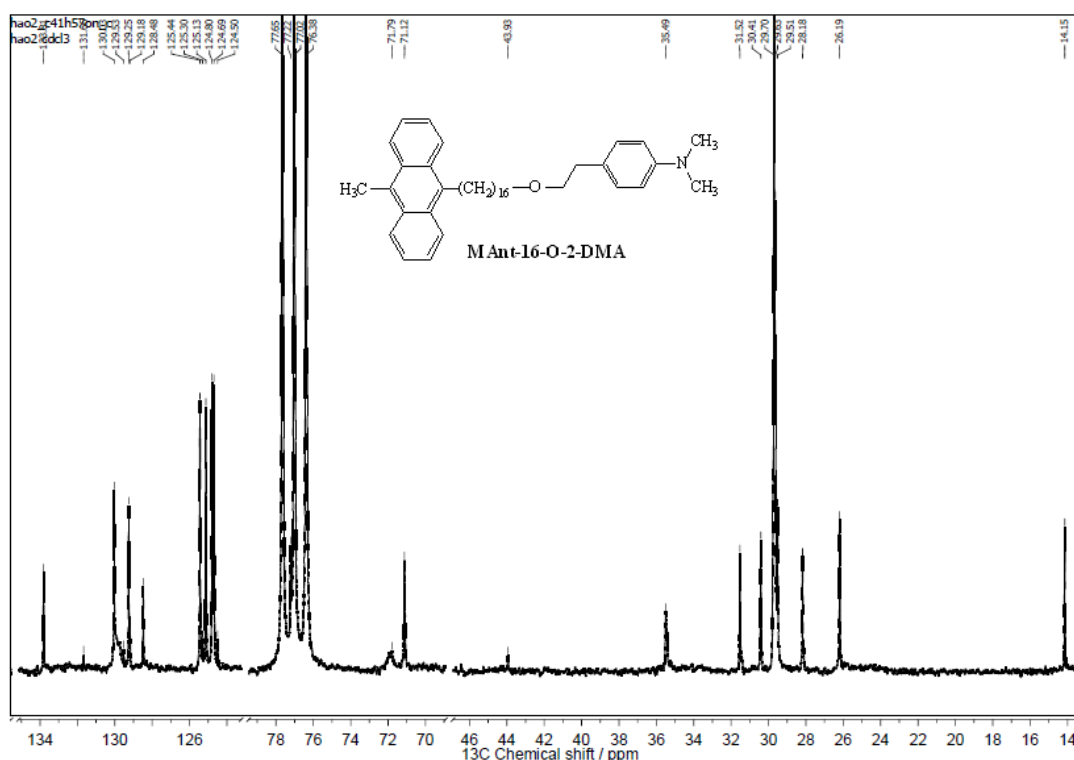


Figure S5i: Proton-decoupled ¹³C-NMR spectrum of 2-[4-(dimethylamino)phenyl]ethyl 16-[9-(10-methyl)anthryl]hexadecyl ether (MAnt-16-O-2-DMA).

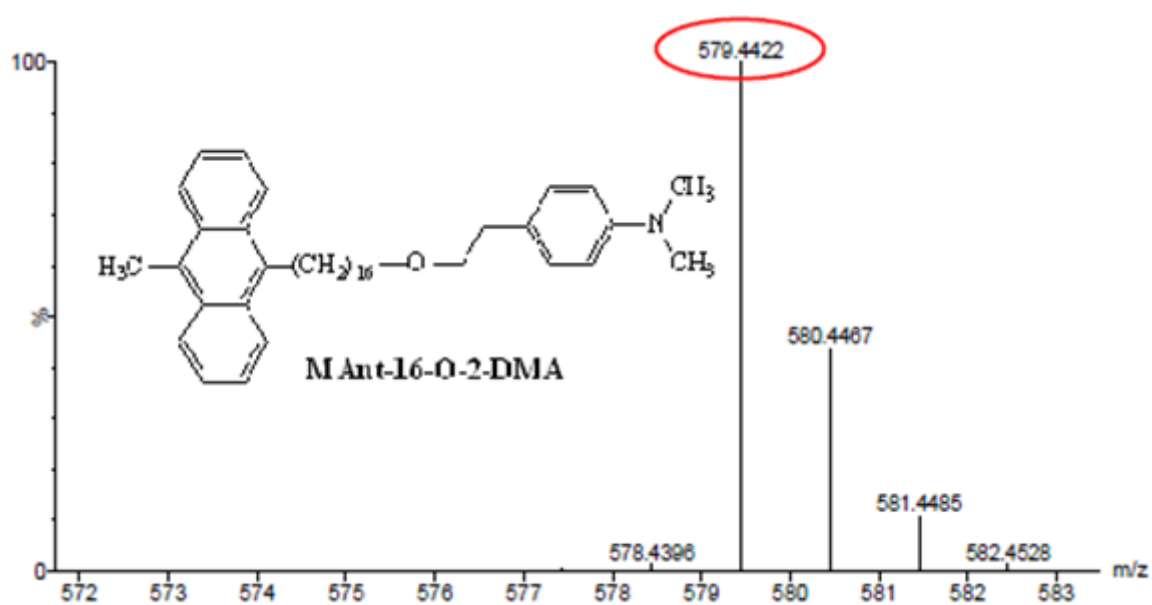


Figure S5j: Mass spectrum of 2-[4-(dimethylamino)phenyl]ethyl 16-[9-(10-methyl)anthryl]hexadecyl ether (MAnt-16-O-2-DMA).

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