J Mater Sci (2007) 42:10228–10238
DOI 10.1007/s10853-007-1634-6

Synthesis and applications of fluoroalkyl end-capped cooligomers having fullerene and mixed fullerenes in the main chain

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Received: 19 November 2006 / Accepted: 20 February 2007 / Published online: 22 September 2007

Abstract Fluoroalkanoyl peroxides reacted with FULLERENES [fullerene (C_{60}) and commercially available fullerenes (Nanom Mix^{TR} and Nanom Black^{TR})] and radical polymerizable comonomers such as acrylic acid, *N,N*-dimethylacrylamide, *N*-(1,1-dimethyl-3-oxobutyl)acrylamide, and acryloylmorpholine to afford fluoroalkyl end-capped cooligomers having FULLERENES in the main chain under very mild conditions. Fluoroalkyl end-capped Nanom Mix and Nanom Black cooligomers thus obtained were found to exhibit a similar solubility to that of the corresponding fluoroalkyl end-capped cooligomers having fullerene in the main chain. These fluorinated FULLERENES cooligomers were found to form the nanometer size-controlled self-assembled cooligomeric aggregates in aqueous solutions. These fluoroalkyl end-capped FULLERENES cooligomers were more effective for solubilizing fullerene, Nanom Mix and Nanom Black into water, compared to those of the corresponding fluoroalkyl end-capped homooligomers having no FULLERENES in the main chain. Fluoroalkyl end-capped fullerene- and Nanom Mix-acrylic acid cooligomers were found to exhibit fluorescence spectra related to fullerene and Nanom Mix in cooligomers, respectively, in aqueous solutions. Additionally, these fluorinated fullerene- and Nanom Mix-acrylic acid cooligomers were able to increase chemiluminescence intensity related to luminol, effectively, compared to the corresponding fluorinated acrylic acid homooligomers.

Introduction

Polymeric fullerene materials have hitherto unveiled a wide range of potential applications in materials science through their interesting properties [1–3]. From a practical point of view, it is of particular interest to study the synthesis of polymeric fullerene materials by the use of not only fullerene (C_{60}) but also commercially available fullerene derivatives. Very recently, preparation of a variety of commercially available fullerene derivatives such as "Nanom Mix"^{TR} and "Nanom Black"^{TR} have been reported [4]. "Nanom Mix"^{TR} is a mixture of C_{60} (60%), C_{70} (25%) and the high order fullerenes (15%), and "Nanom Black"^{TR} is a mixture of fullerene (4%) and carbon (96%) [4]. On the other hand, partially fluorinated polymers, especially fluoroalkyl end-capped oligomers are attractive functional materials due to exhibiting a wide variety of unique characteristics such as a good solubility in various solvents, surface active properties, biological activities, gelling ability, and nanometer size-controlled self-assembled molecular aggregates which cannot be achieved by the corresponding randomly or block-type fluoroalkylated polymers [5]. Therefore, the synthesis of fluoroalkyl end-capped cooligomers containing not only fullerene but also commercially available fullerene derivatives in the main chain is quite interesting from the developmental viewpoints of new fluorinated functional materials possessing unique characteristics imparted by fullerene and its derivatives. However, studies on the synthesis and properties of these polymeric compounds have been hitherto very limited, but these fluorinated polymeric

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materials have been the subjects of considerable research of both a fundamental and applied nature. In a preliminary account, we reported on the synthesis and surfactant properties of fluoroalkyl end-capped cooligomers having fullerene (C_{60}) in the main chain [6]. In this paper, we would like to report on the synthesis and applications of fluoroalkyl end-capped cooligomers having fullerene and commercially available fullerene derivatives such as "Nanom Mix"^{TR} and "Nanom Black"^{TR} in the main chain.

Experimental

Measurements

Molecular weights were measured by using a Shodex DS-4 (Pomp) and Shodex RI-71 (Detector) gel permeation chromatography (GPC; Tokyo, Japan) calibrated with polystyrene standards, using tetrahydrofuran (THF) as the eluent. NMR spectra and Fourier-transform infrared (FT-IR) spectra were measured using a JEOL JNM-400 (400 MHz) FT NMR SYSTEM (Tokyo, Japan) and Shimadzu FTIR-8400 FT-IR spectrophotometer (Kyoto, Japan), respectively. Dynamic light scattering (DLS) was measured using a Otsuka Electronics DLS-7000 HL (Tokyo, Japan). Thermal analyses were recorded on a RIGAKU DENKI TG8101 D differential thermobalance (Tokyo, Japan). Ultraviolet-visible (UV–VIS) spectra were measured using a Shimadzu UV-1600 UV–VIS spectrophotometer (Kyoto, Japan). Fluorescence spectra and chemiluminescence of luminol were measured using a JASCO FP-6300 spectrophotometer (Tokyo, Japan) and Luminescence Reader BLR-201 (Aloka Co., Ltd., Tokyo, Japan), respectively. Transmission electron microscopy was measured by the use of JEOL JEM1210 (Tokyo, Japan).

Materials

Fullerene (C_{60}: purity $> 90\%$) was purchased from Tokyo Kasei Kogyo Co., Ltd (Tokyo, Japan). "Nanom Mix"^{TR} and "Nanom Black"^{TR} were obtained by Frontier Carbon Corporation (Tokyo, Japan). Acrylic acid (ACA), *N*-(1,1-dimethyl-3-oxobutyl)acrylamide (DOBAA) and *N,N*-dimethylacrylamide (DMAA) were used as received from TOAGOSEI Co., Ltd (Tokyo, Japan) and Kohjin Co., Ltd (Tokyo, Japan), respectively. A variety of fluoroalkanoyl peroxides were prepared according to our previously reported methods [7].

Reactions of fluoroalkanoyl peroxides with FULLERENES and comonomers

Following is a typical experimental procedure for the synthesis of fluoroalkyl end-capped cooligommers having FULLERENES in the main chain. Perfluoro-2-methyl-3-oxahexanoyl peroxide (3.3 mmol) in 1:1 mixed solvents (AK-225) of 1,1-dichloro-2,2,3,3,3-pentafluoropropane and 1,3-dichloro-1,2,2,3,3-pentafluoropropane (400 g) was added to the dispersed chlorobenzene solutions (15 ml) containing Nanom Mix (300 mg) and acrylic acid [ACA] (30 mmol). The solution was stirred at 45 °C for 5 h under nitrogen. After the removal of solvent, the obtained crude products were washed well with AK-225, which exhibits a good dispersibility for Nanom Mix to give an α, ω-bis(perfluoro-1-methyl-2-oxapentylated) Nanom Mix-ACA cooligomers [R_F-(Nanom Mix)$_x$-(ACA)$_y$-R_F] (2.68 g).

This cooligomer exhibited the following spectra characteristics:

R_F-(Nanom Mix)$_x$-(ACA)$_y$-R_F:R_F = $CF(CF_3)OC_3F_7$:IR (υ/cm^{-1}) 3452 (OH), 2966 (CH), 1716 (C=O), 1454 (C_{60}), 1411 (CF_3), 1242 (CF_2), 1190 (–C_{60}–), 597 (–C_{60}–), 521 (–C_{60}–); ^{1}H NMR (CD_3OD) δ 1.40–2.10 (CH_2), 2.15–2.65 (CH).

The other products obtained exhibited the following spectral characteristics:

R_F-(C_{60})$_x$-(ACA)$_y$-R_F:R_F = $CF(CF_3)OC_3F_7$:IR (υ/cm^{-1}) 3649 (OH), 2962 (CH), 1716 (C=O), 1454 (C_{60}), 1419 (CF_3), 1242 (CF_2), 1199 (–C_{60}–), 524 (C_{60}); ^{1}H NMR (CD_3OD) δ 1.42–2.05 (CH_2), 2.37–2.50 (CH).

R_F-(Nanom Black)$_x$-(ACA)$_y$-R_F:R_F = $CF(CF_3)OC_3F_7$: IR (υ/cm^{-1}) 3855 (OH), 2928 (CH), 1716 (C=O), 1454 (C_{60}), 1411 (CF_3), 1242 (CF_2); ^{1}H NMR (CD_3OD) δ 1.40–2.20 (CH_2), 2.20–2.65 (CH).

R_F-(C_{60})$_x$-(ACA)$_y$-R_F:R_F = $CF(CF_3)OCF_2CF(CF_3)OC_3F_7$:IR ($\upsilon$/cm^{-1}) 2962 (CH), 1716 (C=O), 1458 (C_{60}), 1419 (CF_3), 1242 (CF_2), 1164 (–C_{60}–), 524 (C_{60}); ^{1}H NMR (CD_3OD) δ 1.40–2.05 (CH_2), 2.30–2.50 (CH).

R_F-(C_{60})$_x$-(DOBAA)$_y$-R_F:R_F = $CF(CF_3)OC_3F_7$:IR (υ/cm^{-1}) 3371 (OH), 2935 (CH_3), 1708 (C=O), 1655, 1365 (CF_3), 1242 (CF_2), 501 (C_{60}); ^{1}H NMR (CD_3OD) δ 1.05–2.45 (CH_2, CH_3), 2.60–3.20 (CH, CH_3).

R_F-(Nanom Mix)$_x$-(DOBAA)$_y$-R_F:R_F = $CF(CF_3)OC_3F_7$: IR (υ/cm^{-1}) 2977 (CH_3), 1716 (C=O), 1655, 1242 (CF_2), 1199 (–C_{60}–); ^{1}H NMR (CD_3OD) δ 1.05–2.60 (CH_2, CH_3), 2.60–3.20 (CH, CH_3).

R_F-(Nanom Black)$_x$-(DOBAA)$_y$-R_F:R_F = $CF(CF_3)OC_3F_7$:IR (υ/cm^{-1}) 3371 (OH), 2977 (CH_3), 1716 (C=O), 1655, 1365 (CF_3), 1242 (CF_2); ^{1}H NMR (CD_3OD) δ 1.05–2.45 (CH_2, CH_3), 2.45–3.25 (CH, CH_3).

R_F-(C_{60})$_x$-(ACMO)$_y$-R_F:R_F = $CF(CF_3)OCF_2CF(CF_3)OC_3F_7$:IR ($\upsilon$/cm^{-1}) 1630 (C=O), 1302 (CF_3), 1243 (CF_2), 1161 (–C_{60}–), 1117 (–O–), 580 (C_{60}), 534 (–C_{60}–); ^{1}H NMR (CD_3OD) δ 0.97–1.99 (CH), 2.27–2.99 (CH_2), 3.15–4.10 (CH).

R_F-(C_{60})$_x$-(DMAA)$_y$-R_F:R_F = $CF(CF_3)OC_3F_7$:IR (υ/cm^{-1}) 3440 (OH), 2943 (CH_3), 1636 (C=O), 1338 (CF_3), 1238

(CF_2), 1199 (C_{60}), 559 (C_{60}), 517 (C_{60}); ^{1}H NMR(CD_3OD) δ 1.05–2.05 (CH, CH_2), 2.35–3.25 (CH_2, CH_3).

Solubilization of FULLERENES into water by the use of fluoroalkyl end-capped cooligomers having FULLERENES in the main chain

To an aqueous solution of fluoroalkyl end-capped fullerene cooligomer [R_F-$(C_{60})_x$-$(ACA)_y$-R_F; $R_F = CF(CF_3)OC_3F_7$; Mn = 5080 (Mw/Mn = 1.85); 2.5 g/dm^3; 2 ml] was added C_{60} (2 mg). The mixture was stirred with a magnetic stirring bar at room temperature for 3 days. The aqueous solution thus obtained was filtered through a 1.2 μm filter membrane to obtain a brownish solution. The relative amounts of solubilized C_{60} in water were estimated by the optical density at 350 nm (UV–Vis spectra) with the use of the molar absorption coefficient (ε) of C_{60}-aqueous solution reported by Yamakoshi et al. and the relative amounts of solubilized C_{60} were recorded [8].

The solubilization of FULLERENES into water by the use of other fluoroalkyl end-capped cooligomers having FULLERENES in the main chain were studied under similar conditions.

Luminol chemiluminescence in the presence of fluoroalkyl end-capped cooligomers having FULLERENES in the main chain

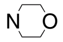
In a typical chemiluminescence study, aqueous solutions of luminol (200 nmol/ml; 200 μl) and $K_3Fe(CN)_6$ (400 μmol/dm^3; 50 μl), R_F-(Nanom Mix)$_x$-(ACA)$_y$-R_F aqueous solution (2 g/dm^3, 450 μl) and 0.2 mol/dm^3 sodium carbonate buffer (pH 11.7; 300 μl) were mixed in a polyethylene tube placed in a chemiluminescence detector at 37 °C. After 1 min, chemiluminescence was initiated by adding an aqueous H_2O_2 solution (100 μmol/dm^3; 100 μl) by an injector to record the light emission time course.

Results and discussion

The reactions of fluoroalkanoyl peroxides with “FULLERNES” (fullerene, Nanom Mix and Nanom Black) and radical polymerizable comonomers such as acrylic acid (ACA), *N*-(1,1-dimethyl-3-oxobutyl)acrylamide (DOBAA) and *N,N*-dimethylacrylamide (DMAA) and acryloylmorpholine (ACMO) were found to proceed under very mild conditions to afford fluoroalkyl end-capped FULLERENES cooligomers in 32 ~ 79% isolated yields. Relatively lower isolated yields (Runs 4 and 8) were obtained in the case of fluoroalkyl end-capped cooligomers having Nanom Black in the main chain. This would be due to the lower purity of fullerene in Nanom Black (see Table 1).

We have tested fluoroalkyl end-capped cooligomers having FULLERENES in the main chain thus obtained for solubility in a variety of solvents at room temperature. Interestingly, a variety of fluorinated FULLERENES cooligomers were found to exhibit a good solubility not only in water but also in common organic solvents such as methanol, ethanol, tetrahydrofuran (THF), chloroform, dimethyl

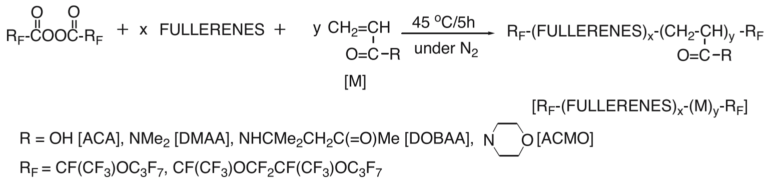
Table 1 Reactions of fluoroalkanoyl peroxide with FULLERENES and comonomers

Run	R_F in $(R_FCO_2)_2$ (mmol)	FULLERENES (mg)	CH_2=CHCOR (mmol)	R_F-(FULLERENES)$_x$-(Co-M)$_y$-R_F	
				Yield(%)^a	Mn(Mw/Mn)^b
	$R_F = CF(CF_3)OC_3F_7$		R = NMe_2		
1	6.5	C_{60}(300)	30	79	2340 (1.48)
	$R_F = CF(CF_3)OC_3F_7$		R = OH		
2	6.5	C_{60}(300)	30	44	2270 (1.26)
3	6.5	Nanom Mix (300)	30	44	3460 (1.38)
4	6.5	Nanom Black (300)	30	41	3340 (1.30)
	$R_F = CF(CF_3)OCF_2CF(CF_3)OC_3F_7$				
5	3.3	C_{60}(150)	15	32	2280 (1.30)
	$R_F = CF(CF_3)OC_3F_7$		R = $NHCMe_2CH_2C(=O)Me$		
6	3.4	C_{60}(300)	11	57	5310 (1.82)
7	3.4	Nanom Mix (300)	11	77	5650 (1.51)
8	3.4	Nanom Black (300)	11	54	5040 (1.35)
	$R_F = CF(CF_3)OCF_2CF(CF_3)OC_3F_7$		R = 		
9	3.3	C_{60}(150)	12	62	6520 (1.34)

[a] The yields are based on the starting materials [C_{60} (Nanom Mix or Nanom Black), comonomers and the decarboxylated peroxide unit (R_F–R_F)]

[b] Molecular weight of cooligomer was determined by GPC

Scheme 1



sulfoxide (DMSO), *N, N*-dimethylformamide (DMF) and a fluorinated solvent [1:1 mixed solvents (AK-225) of 1,1-dichloro-2,2,3,3,3-pentafluoropropane and 1,3-dichloro-1,2,2,3,3-pentafluoropropane], although fluoroalkyl end-capped FULLERENES–DOBAA cooligomers have no solubility in water and the parent FULLERENES exhibited no solubility in water, ethanol, THF and DMF. Therefore, we can easily measure the molecular weights of these fluoroalkyl end-capped FULLERENES cooligomers by GPC using THF as the eluent, and the obtained values (Mn) were 2,300–6,500 (see Scheme 1 and Table 1).

In order to clarify the presence of FULLERENES in fluoroalkyl end-capped cooligomers, we have analyzed these fluorinated cooligomers by the use of thermogravimetric analyses (TGA) measurements, in which the weight loss of these cooligomers were measured by raising the temperature around to 800 °C, and the results are shown in Figs. 1–3 and Table 2.

As shown in Figs. 1–3, the thermal stability of fluoroalkyl end-capped acrylic acid cooligomers containing FULLERENES in the main chain was found to decrease compared to that of the parent FULLERENES; however their thermal stability was superior to that of the corresponding fluoroalkyl end-capped homooligomers containing no FULLERENES in the main chain. This finding is due to the introduction of FULLERENES in the fluoroalkyl end-capped oligomeric main chain. The contents of FULLERENES in the product was estimated to be 5–6% by the use of the TGA data in Figs. 1–3. The thermal stability and the contents of FULLERENES in the other fluorinated cooligomers were also estimated under similar

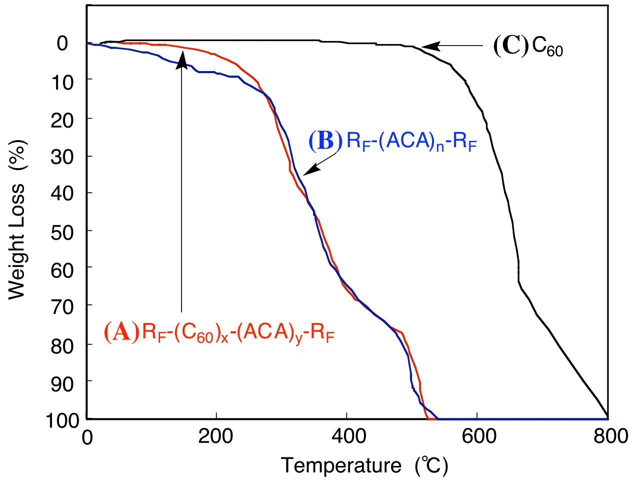


Fig. 1 Thermogravimetric analyses of (A) R_F-$(C_{60})_x$-$(ACA)_y$-R_F cooligomer [Mn = 2270 (Mw/Mn = 1.26)] (B) R_F-$(ACA)_n$-R_F [Mn = 2770 (Mw/Mn = 1.58)], and (C) C_{60} $R_F = CF(CF_3)OC_3F_7$

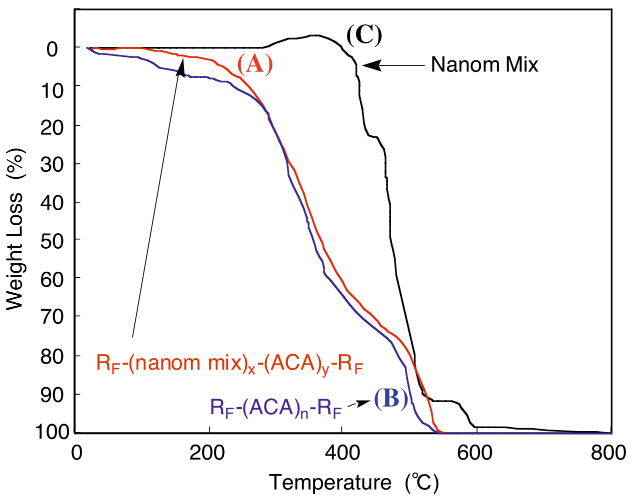


Fig. 2 Thermogravimetric analyses of (A) R_F-(Nanom Mix)$_x$-$(ACA)_y$-R_F cooligomer [Mn = 3460 (Mw/Mn = 1.38)], (B) R_F-$(ACA)_n$-R_F [Mn = 2770 (Mw/Mn = 1.58)], and (C) Nanom Mix $R_F = CF(CF_3)OC_3F_7$

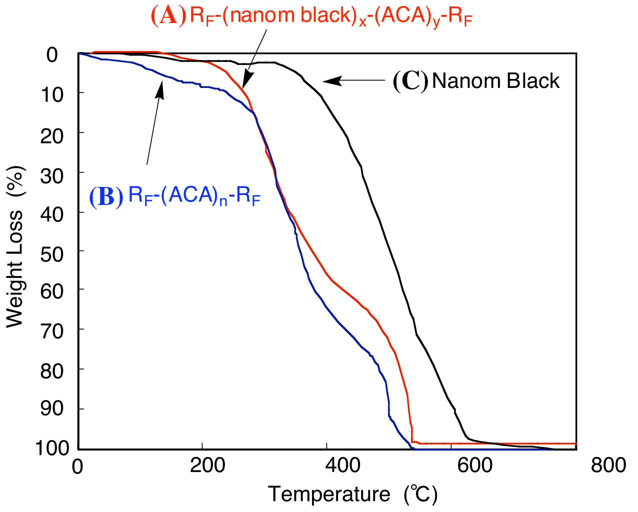


Fig. 3 Thermogravimetric analyses of (A) R_F-(Nanom Black)$_x$-$(ACA)_y$-R_F cooligomer [Mn = 3340 (Mw/Mn = 1.30)], (B) R_F-$(ACA)_n$-R_F [Mn = 2770 (Mw/Mn = 1.58)], and (C) Nanom Black $R_F = CF(CF_3)OC_3F_7$

Table 2 Contents of FULLERENES in fluoroalkyl end-capped FULLERENES cooligomers determined by TGA measurements [$R_F = CF(CF_3)OC_3F_7$]

Run	Oligomer [Mn]	Content of FULLERENES in cooligomer [%(wt)]
1[a]	R_F-$(C_{60})_x$-$(ACA)_y$-R_F[5080]	2
2	R_F-$(C_{60})_x$-$(ACA)_y$-R_F[2270]	5
3[b]	R_F-$(C_{60})_x$-$(ACA)_y$-R_F[2280]	2
4	R_F-$(C_{60})_x$-$(DMAA)_y$-R_F[2340]	4
5[b]	R_F-$(C_{60})_x$-$(ACMO)_y$-R_F[6520]	6
6	R_F-$(C_{60})_x$-$(DOBAA)_y$-R_F[5310]	2
7	R_F-(Nanom Mix)$_x$-$(ACA)_y$-R_F[3460]	5
8	R_F-(Nanom Black)$_x$-$(ACA)_y$-R_F[3340]	6
9	R_F-(Nanom Mix)$_x$-$(DOBAA)_y$-R_F[5650]	3
10	R_F-(Nanom Black)$_x$-$(DOBAA)_y$-R_F[5040]	1

[a] This cooligomer was prepared in a large scale according to the described method in Table 1 (Run 2)

[b] $R_F = CF(CF_3)OCF_2CF(CF_3)OC_3F_7$

conditions, and the results were illustrated in Table 2. From the TGA data, the contents of FULLERENES in these fluorinated cooligomers were estimated to be 1–6% (see Table 2).

Previously, we reported that fluoroalkyl end-capped homooligomers could form self-assembled molecular aggregates with nanometer size levels in aqueous and organic media [9]. Thus, our present fluorinated FULLERENES cooligomers are expected to form self-assembled molecular aggregates in aqueous and organic media. The size of fluorinated molecular aggregates formed by fluorinated FULLERENES cooligomers were measured by dynamic light scattering measurements at 20 °C. These results were shown in Table 3.

The size (number-average diameter: 16–426 nm) of fluorinated molecular aggregates formed by fluoroalkyl end-capped FULLERENES cooligomers in aqueous and methanol solutions was found to become higher than that (10–24 nm levels) of the corresponding homooligomers. The increase of the size in fluorinated cooligomeric aggregates suggests that FULLERENES should be conclusively introduced into the oligomeric main chain.

Our present fluorinated FULLERENES cooligomers were clarified to form the self-assembled fluorinated cooligomeric aggregates. These fluorinated molecular assemblies should interact with FULLERENES as guest molecules through the van der Waals interactions to exhibit a good solubility in water. Thus, we have studied on the solubilization of FULLERENES into water by the use of

Table 3 Size of fluoroalkyl end-capped oligomeric aggregates and FULLERENES/fluoroalkyl end-capped oligomer nanocomposites in aqueous solutions [$R_F = CF(CF_3)OC_3F_7$][a]

Run	Oligomer [Mn]	FULLERENES in nanocomposites	Cooligomeric aggregates (FULLERENES/oligomeric aggregates) (nm)
1	R_F-$(C_{60})_x$-$(ACA)_y$-R_F [5080]	C_{60}	21.5 ± 2.1 (268.9 ± 34.1)
2	R_F-$(C_{60})_x$-$(ACA)_y$-R_F [2270]	C_{60}	24.8 ± 2.6 (151.4 ± 33.8)
3	R_F-$(ACA)_n$-R_F [2770]	C_{60}	10.4 ± 0.7 (225.0 ± 28.1)
4[b]	R_F-$(C_{60})_x$-$(ACA)_y$-R_F [2280]	C_{60}	24.4 ± 2.4 (145.6 ± 31.9)
5[b]	R_F-$(ACA)_n$-R_F [2630]	C_{60}	11.5 ± 1.4 (65.9 ± 8.6)
6	R_F-$(C_{60})_x$-$(DMAA)_y$-R_F [2340]	C_{60}	31.5 ± 5.7 (142.3 ± 28.1)
7	R_F-$(DMAA)_n$-R_F [4820]	C_{60}	24.1 ± 4.3 (77.7 ± 10.5)
8[b]	R_F-$(C_{60})_x$-$(ACMO)_y$-R_F[6520]	C_{60}	51.4 ± 6.5 (256.7 ± 47.7)
9[b]	R_F-$(ACMO)_n$-R_F [7560]	C_{60}	13.1 ± 0.0 (183.8 ± 35.7)
10	R_F-(Nanom Mix)$_x$-$(ACA)_y$-R_F [3460]	Nanom Mix	24.6 ± 2.5 (219.8 ± 51.2)
11	R_F-$(ACA)_n$-R_F [2770]	Nanom Mix	11.5 ± 1.4 (124.3 ± 31.0)
12	R_F-(Nanom Black)$_x$-$(ACA)_y$-R_F [3340]	Nanom Black	16.1 ± 1.9 (145.7 ± 37.6)
13	R_F-$(ACA)_n$-R_F [2770]	Nanom Black	11.5 ± 1.4 (131.7 ± 30.7)
14[c]	R_F-$(C_{60})_x$-$(DOBAA)_y$-R_F [5310]	–	124.0 ± 11.9
15[c]	R_F-(Nanom Mix)$_x$-$(DOBAA)_y$-R_F [5650]	–	206.5 ± 30.9
16[c]	R_F-(Nanom Black)$_x$-$(ACA)_y$-R_F[5040]	–	426.1 ± 43.9
17[c]	R_F-$(DOBAA)_n$-R_F[12000]	–	11.3 ± 2.3

[a] Solubilization conditions: used FULLERENES: 2 mg; room temperature for 3 days

[b] $R_F = CF(CF_3)OCF_2CF(CF_3)OC_3F_7$

[c] in methanol

fluoroalkyl end-capped FULLERENES cooligomers. These results were shown in Figs. 4–6 and Table 4.

As shown in Fig. 4, UV–VIS spectra of solubilized fullerene into water by R_F-$(C_{60})_x$-$(ACA)_y$-R_F showed an absorption peak around 340 nm. The amounts of solubilized fullerenes were estimated by the use of the molar absorption coefficient (ε): 49,000 (340 nm) of fullerene cited in the case of poly(vinylpyrrolidone) [8], and the solubilized fullerene was 133 μg/ml (see Run 1 in Table 4). The amounts of solubilized Nanom Mix and Nanom Black were also estimated by the use of UV–VIS spectra under similar conditions, these results were shown in Figs. 5 and 6 and Table 4 (see Runs 10, 12 in Table 4).

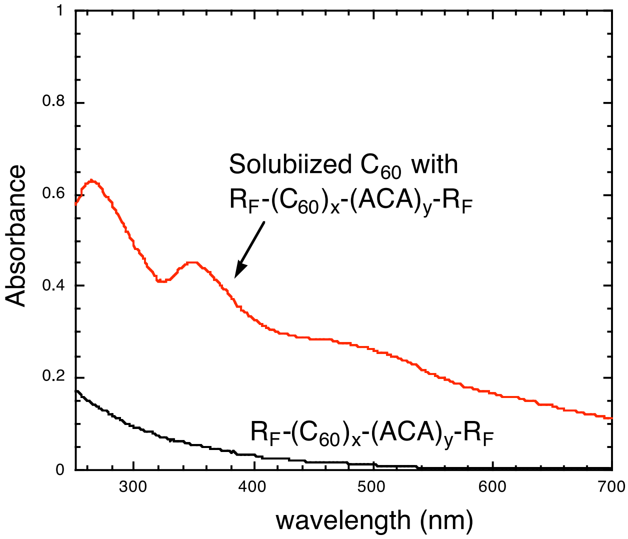


Fig. 4 UV–Vis spectra of aqueous solution of R_F-$(C_{60})_x$-$(ACA)_y$-R_F cooligomer [$R_F = CF(CF_3)OC_3F_7$] in the presence of fullerene Concentration of R_F-$(C_{60})_x$-$(ACA)_y$-R_F: 0.13 g/dm^3

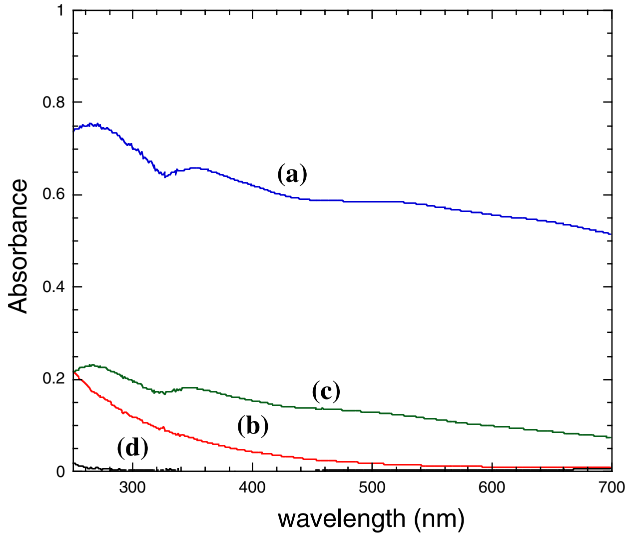


Fig. 5 UV–Vis spectra of aqueous solution of Nanom Mix in the presence of fluoroalkyl end-capped oligomers (Concentration of oligomer: 0.25 g/dm^3) (**a**) R_F-(Nanom Mix)$_x$-$(ACA)_y$-R_F; $R_F = CF(CF_3)OC_3F_7$ (Mn = 3460) in the presence of Nanom Mix (**b**) R_F-(Nanom Mix)$_x$-$(ACA)_y$-R_F; $R_F = CF(CF_3)OC_3F_7$ (Mn = 3460) (**c**) R_F-$(ACA)_n$-R_F; $R_F = CF(CF_3)OC_3F_7$ (Mn = 2770) in the presence of Nanom Mix (**d**) R_F-$(ACA)_n$-R_F; $R_F = CF(CF_3)OC_3F_7$ (Mn = 2770)

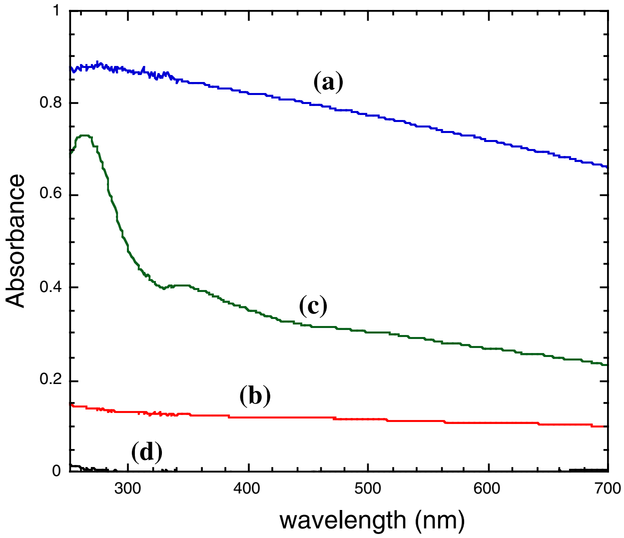


Fig. 6 UV–Vis spectra of aqueous solution of Nanom Black in the presence of fluoroalkyl end-capped oligomers (Concentration of oligomer: 0.25 g/dm^3) (**a**) R_F-(Nanom black)$_x$-$(ACA)_y$-R_F; $R_F = CF(CF_3)OC_3F_7$ (Mn = 3340) in the presence of Nanom Black (**b**) R_F-(nanom black)$_x$-$(ACA)_y$-R_F; $R_F = CF(CF_3)OC_3F_7$ (Mn = 3340) (**c**) R_F-$(ACA)_n$-R_F; $R_F = CF(CF_3)OC_3F_7$ (Mn = 2770) in the presence of Nanom Black (**d**) R_F-$(ACA)_n$-R_F; $R_F = CF(CF_3)OC_3F_7$ (Mn = 2770)

In R_F-$(C_{60})_x$-$(ACA)_y$-R_F [$R_F = CF(CF_3)OCF_2CF(CF_3)OC_3F_7$] cooligomer, the amounts of solubilized fullerene were increased by increasing the stirring times from 1 day to 7 days at room temperature, and almost constant values (ca. 400 μg/ml) were obtained above 6 days as shown in Fig. 7, and the amounts of solubilized fullerenes were higher than those of the corresponding fluorinated homooligomer. Similarly, the amounts of solubilized fullerenes were found to increase with the increase of the concentrations of R_F-$(C_{60})_x$-$(ACA)_y$-R_F from 0.5 g/dm^3 to 6 g/dm^3, and almost constant values (ca. 320 μg/ml) were obtained above 3 g/dm^3, indicating that this concentration (3 g/dm^3) would be essential for the formation of self-assembled fluorinated cooligomeric aggregates (see Fig. 8).

Fluoroalkyl end-capped Nanom Mix- and Nanom Black-acrylic acid cooligomers were also solubilized Nanom Mix (86 μg/ml; see Fig. 5 and Run 10 in Table 4) and Nanom Black (97 μg/ml; see Fig. 6 and Run 12 in Table 4) into water, respectively. Interestingly, fluoroalkyl end-capped FULLERENES-acrylic acid cooligomers were able to solubilize effectively FULLERENES into water, compared to those of the corresponding fluoroalkyl end-capped acrylic acid homooligomers as shown in

Table 4 Solubilization of FULLERENES into water with fluoroalkyl end-capped oligomers [R_F = $CF(CF_3)OC_3F_7$][a]

Run	Oligomer [Mn]	FULLERENES	Solubilized FULLERENES (μg/ml)
1	R_F-$(C_{60})_x$-$(ACA)_y$-R_F [5080]	C_{60}	133
2	$R_F$$(C_{60})_x$-$(ACA)_y$-$R_F$ [2270]	C_{60}	366
3	R_F-$(ACA)_n$-R_F [2770]	C_{60}	83
4[b]	R_F-$(C_{60})_x$-$(ACA)_y$-R_F [2280]	C_{60}	128
5[b]	R_F-$(ACA)_n$-R_F [2630]	C_{60}	40
6	R_F-$(C_{60})_x$-$(DMAA)_y$-R_F [2340]	C_{60}	165
7	R_F-$(DMAA)_n$-R_F [4820]	C_{60}	81
8[b]	$R_F$$(C_{60})_x$-$(ACMO)_y$-$R_F$ [6520]	C_{60}	209
9[b]	R_F-$(ACMO)_n$-R_F [7560]	C_{60}	161
10	R_F-(Nanom Mix)$_x$-$(ACA)_y$-R_F [3460]	Nanom Mix	86
11	R_F-$(ACA)_n$-R_F [2770]	Nanom Mix	37
12	R_F-(Nanom Black)$_x$-$(ACA)_y$-R_F [3340]	Nanom Black	97
13	R_F-$(ACA)_n$-R_F [2770]	Nanom Black	82

[a] Solubilization conditions: used FULLERENES: 2 mg; room temperature for 3 days

[b] R_F = $CF(CF_3)OCF_2CF(CF_3)OC_3F_7$

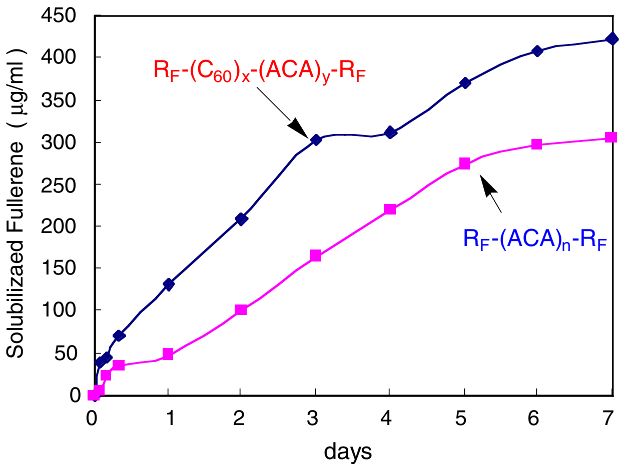


Fig. 7 Relationship between the amounts of solubilized fullerene into the water and the solubilization time. Fluoroalkyl end-capped oligomer: R_F-$(C_{60})_x$-$(ACA)_y$-R_F, R_F-$(ACA)_n$-R_F [R_F = $CF(CF_3)OCF_2$ $CF(CF_3)OC_3F_7$] Concentration of oligomer: 2.5 g/dm^3 (2 ml) Used fullene: 2 mg

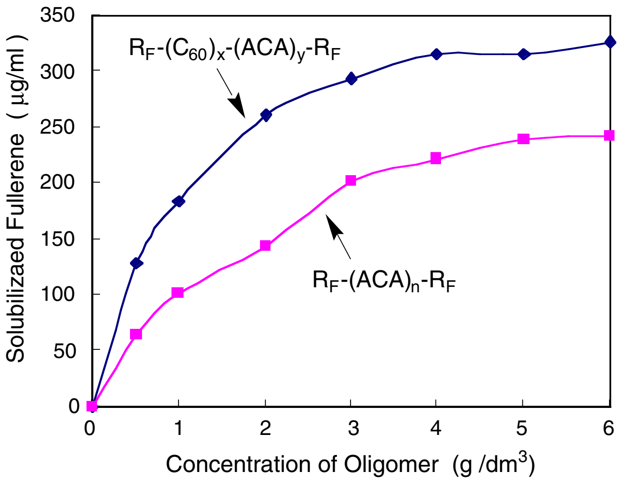


Fig. 8 Relationship between the amounts of solubilized fullerene into water and the concentration of fluorinated oligomer Fluoroalkyl end-capped oligomer: R_F-$(C_{60})_x$-$(ACA)_y$-R_F, R_F-$(ACA)_n$-R_F [R_F = $CF(CF_3)OCF_2CF(CF_3)OC_3F_7$] Used fullerene: 2 mg Condition: r.t/ 3 days

Figs. 4–6, and Runs 1–5, 10–13 in Table 4. Similarly, other fluoroalkyl end-capped fullerene-DMAA and -ACMO cooligomers were able to solubilize fullerene more effectively into water than those of the corresponding homooligomers (see Runs 6–9 in Table 4). These findings suggest that FULLERENES should be tightly encapsulated into fluorinated FULLERENES cooligomeric aggregates cores through the van der Waals interaction between the FULLERENES segments in aggregate cores and guest molecules (FULLERENES) in aqueous media.

Table 3 shows that the size of fluorinated FULLERENES cooligomers and fluorinated homooligomers were found to increase from 16–51 nm (cooligomers) and 10–24 nm (homooligomers) to 142–269 nm (cooligomers) and 66–225 nm (homooligomers) by the solubilization of FULLERENES into water, respectively. The increase of the size of FULLERENES/fluorinated co- and homo-oligomers composites formed by the solubilization of FULLERENES into water indicates that FULLERENES should be encapsulated in the self-assemblies of fluorinated

FULLERENES cooligmers and fluorinated homooligomers to afford stable FULLERENES/fluorinated co- and homo-oligomers nanocomposites in aqueous solutions. In particular, it was clarified that fluorinated FULLERENES cooligomers were more effective for the solubilization of FULLERENES and the increase of the size of the obtained nanocomposites in water, compared to those of the corresponding fluorinated homooligomers, indicating that FULLERENES should be strongly interacted with FULLERENES segments in fluorinated cooligomeric aggregate cores through the van der Waals interaction to increase both the solubilization ratios of FULLERENES and the nanocomposite size in water. Transmission electron microscopy (TEM) images of freshly prepared samples of FULLERENES/R_F-(FULLERENES)$_x$-(ACA)$_y$-R_F nanocomposites and C_{60}/R_F-(ACA)$_n$-R_F homooligomer nanocomposites under similar conditions were shown in Figs. 9–12.

Figures 9–12 shows the formation of nanometer size-controlled C_{60}/R_F-(C_{60})$_x$-(ACA)$_y$-R_F, C_{60}/R_F-(ACA)$_n$-R_F, and Nanom Mix/R_F-(Nanom Mix)$_x$-(ACA)$_y$-R_F nanocomposites. These nanocomposites were also found to be very fine spheres. On the other hand, it was demonstrated that Nanom Black/R_F-(Nanom Black)$_x$-(ACA)$_y$-R_F nanocomposite is likely to suffer the agglomeration of the nanoparticles during sample preparation for TEM measurements, due to the higher contents of carbon in this nanocomposites (see Fig. 12).

Our present fluorinated FULLERENES cooligomers were demonstrated to form the nanometer size-controlled

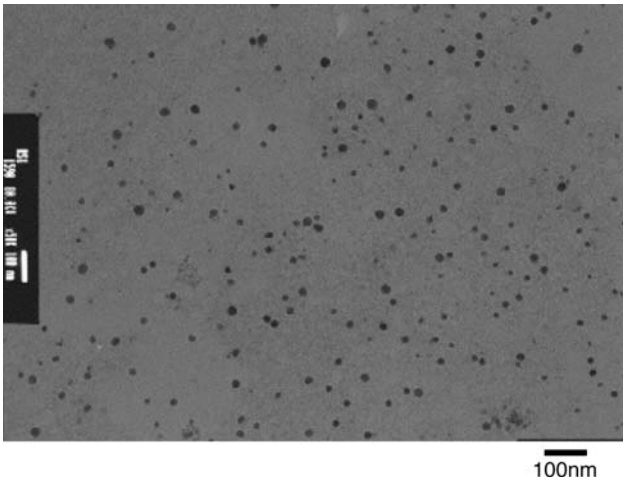


Fig. 9 TEM (Transmission Electron Microscopy) image of C_{60}/R_F-(C_{60})$_x$-(ACA)$_y$-R_F [R_F = CF(CF_3)OC_3F_7] (Mn = 2270) nanocomposites (see Run 2 in Table 4) in aqueous solutions

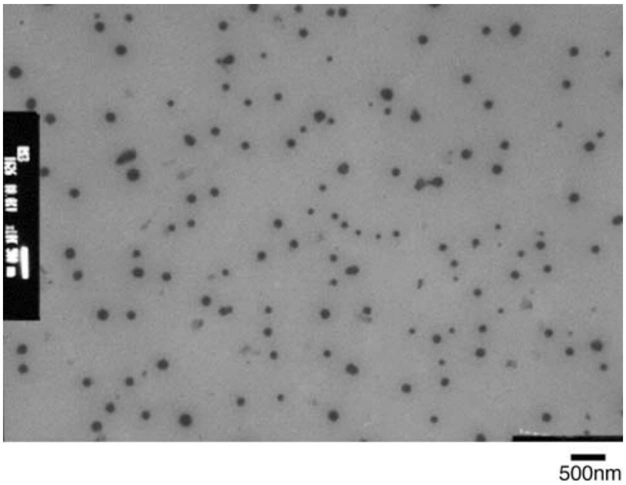


Fig. 11 TEM image of Nanom Mix/R_F-(Nanom Mix)$_x$-(ACA)$_y$-R_F nanocomposites (see Run 10 in Table 4) in aqueous solutions

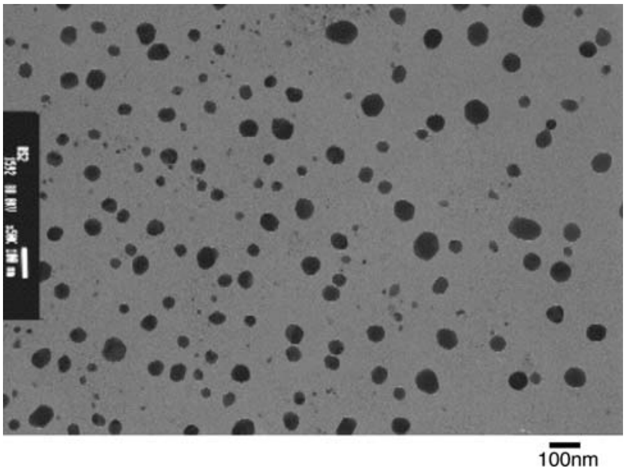


Fig. 10 TEM image of C_{60}/R_F-(ACA)$_n$-R_F nanocomposites (see Run 3 in Table 4)in aqueous solutions

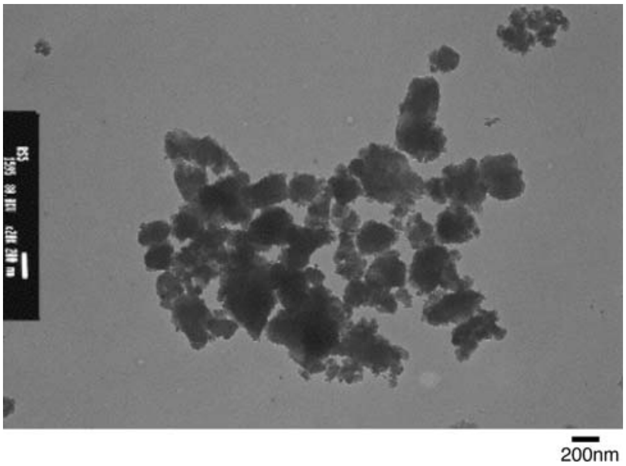


Fig. 12 TEM image of Nanom Black/R_F-(Nanom Black)$_x$-(ACA)$_y$-R_F nanocomposites (see Run 12 in Table 4) in aqueous solutions)

fluorinated cooligomeric aggregates. Therefore, these fluorinated oligomeric aggregates are expected to exhibit fluorescence spectra related to FULLERENES in cooligomeric aggregate cores in aqueous solutions. Thus, we tried to measure the fluorescence spectra of fluoroalkyl end-capped FULLERENES-acrylic acid cooligomers in aqueous solutions, and the results were shown in Fig. 13.

When the solutions are excited ($\lambda = 350$ nm) into the intense absorption bands in the UV–VIS region, fluorinated C_{60}-ACA and Nanom Mix-ACA cooligomers emit fluorescence with a peak maximum around 540 nm; however, fluorinated Nanom Black-ACA cooligomer have no fluorescence spectra at all under these conditions as shown in Fig. 13. The highest fluorescent intensity was obtained in fluorinated C_{60}-ACA cooligomer, indicating that this fluorinated cooligomer could possess pure C_{60} segments in the main chain, compared to other fluorinated FULLERENES cooligomers. We have also studied the relationship between the fluorescence intensity and the concentration of R_F-$(C_{60})_x$-$(ACA)_y$-R_F cooligmer, and the results were shown in Fig. 14.

Fluorescent intensity related to C_{60} in cooligomers was found to increase with the increase of the concentration of coligomer. On the other hand, interestingly, fluorescent intensity related to C_{60} was found to increase extremely with increase the concentration of C_{60} in C_{60}/R_F-$(C_{60})_x$-$(ACA)_y$-R_F nanocomposites, compared to that of the corresponding R_F-$(C_{60})_x$-$(ACA)_y$-R_F cooligomer. However, fluorescent intensity of C_{60}/R_F-$(C_{60})_x$-$(ACA)_y$-R_F nanocomposites was extraordinarily decreased above 9 μg/ml of C_{60} in the nanocomposites, indicating that C_{60}s in the nanocomposites are likely to have self-quenching in the fluorinated cooligomeric aggregate cores under these conditions. A similar result was obtained in R_F-(Nanom Mix)$_x$-$(ACA)_y$-R_F and Nanom-Mix/R_F-(Nanom Mix)$_x$-$(ACA)_y$-R_F nanocomposites as in Fig. 15, and fluorescence intensity related to Nanom Mix in cooligomer and the nanocomposites were found to increase with the increase of the concentrations of both cooligomer and Nanom Mix in nanocomposites. Especially, the highest fluorescent intensity was observed at the concentration of 9 μg/ml of Nanom Mix in the nanocomposite.

In this way, it was verified that our present fluorinated FULLERENES cooligomers can form the nanometer size-

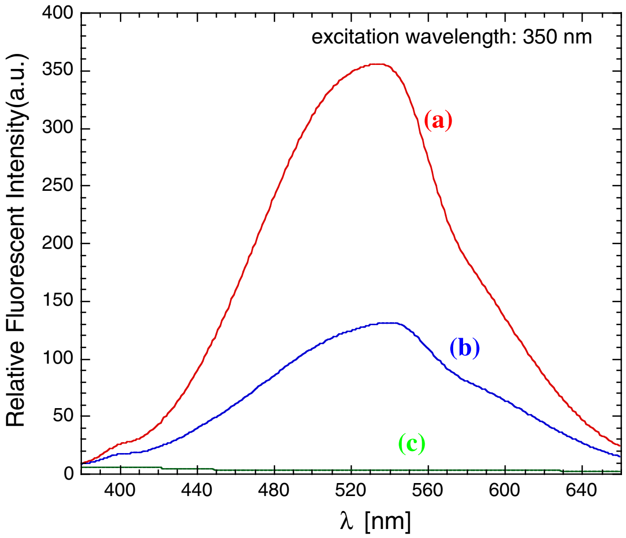


Fig. 13 Fluorescence spectra of aqueous solutions of fluoroalkyl end-capped FULLERENES cooligomers [Concentration of cooligomer: 2 g/dm^3 $R_F = CF(CF_3)OC_3F_7$] (**a**) R_F-$(C_{60})_x$-$(ACA)_y$-R_F [Mn = 5080] (**b**) R_F-(Nanom Mix)$_x$-$(ACA)_y$-R_F (**c**) R_F-(Nanom Black)$_x$-$(ACA)_y$-R_F

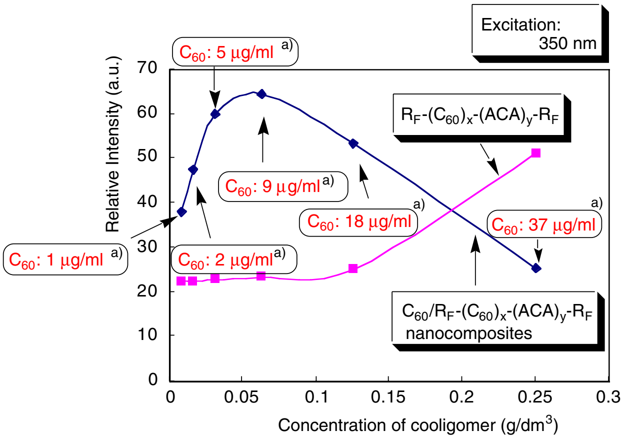


Fig. 14 Relationship between the fluorescent intensity of C_{60} in R_F-$(C_{60})_x$-$(ACA)_y$-R_F (including C_{60} in C_{60}/R_F-$(ACA)_y$-R_F nanocomposites) and the concentrations of R_F-$(C_{60})_x$-$(ACA)_y$-R_F; Mn = 5080, $R_F = CF(CF_3)OC_3F_7$ a) Concentrations (1–37 μg/ml) of C_{60} indicate those of C_{60} in the C_{60}/R_F-$(C_{60})_x$-$(ACA)_y$-R_F nanocomposites

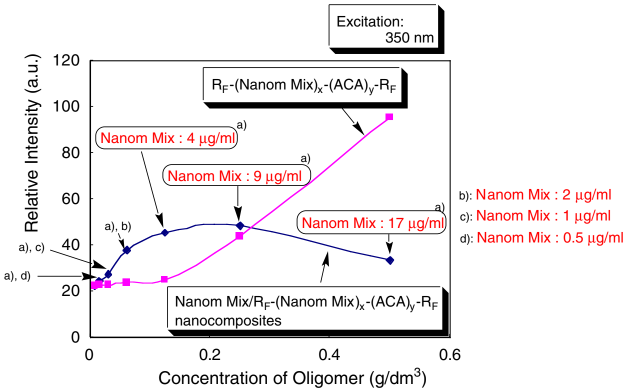
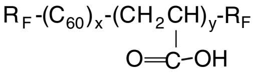
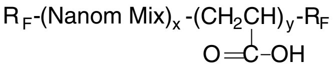
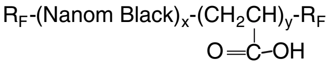
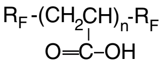


Fig. 15 Relationship between the fluorescent intensity of Nanom Mix in R_F-(Nanom Mix)$_x$-$(ACA)_y$-R_F (including Nanom Mix in Nanom Mix/R_F-(Nanom-Mix)$_x$-$(ACA)_y$-R_F nanocomposites) and the concentrations of R_F-(Nanom Mix)$_x$-$(ACA)_y$-R_F; $R_F = CF(CF_3)OC_3F_7$ (a) Concentrations (0.5–17 μg/ml) of Nanom Mix indicate those of Nanom Mix in the Nanom Mix/R_F-(Nanom Mix)$_x$-$(ACA)_y$-R_F nanocomposites

Table 5 Light intensity of luminol in the presence of fluoroalkyl end-capped FULLERENES-ACA cooligomers

Oligomer	Light Intensity ($\times 10^{-3}$ counts/30 min)
 $R_F\text{-}(C_{60})_x\text{-}(CH_2\underset{O{=}C\text{-}OH}{CH})_y\text{-}R_F$ [Mn = 2270]	8100
 $R_F\text{-}(\text{Nanom Mix})_x\text{-}(CH_2\underset{O{=}C\text{-}OH}{CH})_y\text{-}R_F$	12600
 $R_F\text{-}(\text{Nanom Black})_x\text{-}(CH_2\underset{O{=}C\text{-}OH}{CH})_y\text{-}R_F$	2100
 $R_F\text{-}(CH_2\underset{O{=}C\text{-}OH}{CH})_n\text{-}R_F$	7200

$R_F = CF(CF_3)OC_3F_7$

Final concentration: 0.2 mmol/dm^3 Na_2CO_3 buffer [300 μdm^3]; 2 g/dm^3 Oligomer Solution [450 μdm^3]; 0.4 mmol/dm^3 $K_3Fe(CN)_6$ [50 μdm^3]; 200 nmol/ml Luminol [200 μdm^3]; 100 μmol/dm^3 H_2O_2 [100 μdm^3]

controlled self-assembled molecular aggregates, and these fluorinated molecular aggregates could afford fluorescent spectra related to FULLERENES in aqueous solutions. Therefore, the well-known chemiluminescent compounds such as luminol are potential guest molecules for these fluorinated cooligomeric aggregates to enhance chemiluminescence intensity. In fact, we tried to study the luminol chemiluminescence in the presence of R_F-(FULLERENES)$_x$-(ACA)$_y$-R_F cooligomers, and the results were shown in Table 5.

R_F-$(C_{60})_x$-(ACA)$_y$-R_F and R_F-(Nanom Mix)$_x$-(ACA)$_y$-R_F were found to enhance dramatically the light emission yield, while R_F-(Nanom Black)$_x$-(ACA)$_y$-R_F and the corresponding fluoroalkyl end-capped acrylic acid homooligomer [R_F-(ACA)$_n$-R_F] decreased the light yield. These observations indicate that the R_F-$(C_{60})_x$-(ACA)$_y$-R_F and R_F-(Nanom Mix)$_x$-(ACA)$_y$-R_F cooligomeric aggregate cores are essential in cooligomers enhancing luminol chemiluminescence light yield. These fluorinated cooligomeric aggregate cores provide hydrophobic environment to the guest, luminal. The fluorescent quantum yield of the light emitter is often increased by changing the environment from hydrophilic to hydrophobic [10–14]. The fluorescent quantum yield of the light emitter of luminol chemiluminescence should be increase more effectively through the energy transfer from the singlet excited sodium 3-aminophthalate, the light emitter of luminol chemiluminescence, to FULLERENES segments in the fluorinated C_{60} and Nanom Mix cooligomeric aggregates cores. In contrast, in the case of R_F-(Nanom Black)$_x$-(ACA)$_y$-R_F, the chemiluminescence intensity would be extremely decreased due to the quenching of Nanom Black in cooligomer toward the singlet excited sodium 3-aminophthalate.

In conclusion, it was demonstrated that fluoroalkanoyl peroxides is a convenient initiator for preparation of fluoroalkyl end-capped cooligomers having FULLERENES in the main chain under very mild conditions. Fluoroalkyl end-capped FULLERENES cooligomers thus obtained exhibited a higher thermal stability than that of the corresponding fluorinated homooligomers having no FULLERENES. Hitherto, applications of fullerenes into not only the biomedical but also the other various fields have been very limited owing to their poor solubility in polar solvents including water [15]. In contrast, our present these fluorinated FULLERENES cooligomers had a good solubility not only in water but also in common organic solvents, and were able to form the nanometer size-controlled self-assembled fluorinated cooligomeric aggregates. These fluorinated FULLERENES cooligomers were able to solubilize FULLERENES into water, quite effectively, compared to that of the corresponding fluorinated homooligomers having no FULLERENES, suggesting that FULLERENES should be tightly encapsulated as guest molecules into the fluorinated cooligomeric aggregates cores. Fluorinated C_{60}- and Nanom Mix-ACA cooligomers were found to exhibit fluorescence spectra related to the original C_{60} and Nanom Mix, although the fluorinated Nanom Black-ACA cooligomer had no fluorescence spectra related to Nanom Black under these conditions. Additionally, fluorinated C_{60}- and Nanom Mix-ACA cooligomers can form unique host molecular aggregates accommodating luminol and potentially enhancing light emission yield in the chemiluminescence in aqueous solutions compared to that of the corresponding fluorinated ACA homooligomers. Therefore, our present fluorinated FULLERENES cooligomers could open new developments in fullerenes chemistry.

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